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Biogeochemical Nature of Mercury in Forested Soils

by

© Karen Rachel Cannon

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

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ABSTRACT

Two deciduous forested areas near Edmonton were studied for a two year period to ascertain the seasonal fluctuation in the natural abundance of mercury in litter layers. Inputs of mercury were assessed by monitoring levels of mercury in forest vegetation, in rainfall, in dry deposition, and in soil gases at various times of the year. Levels of mercury in forest litter were also monitored as it decomposed under field and laboratory conditions to assess possible loss or negative enrichment. The form of mercury present in organic surface soils was determined by a pyrolysis experiment.

Levels of mercury in L, F, and H horizons sampled in early spring were 81, 129, and 63 ppb Hg, respectively, and were generally lower in June and July and decreased to minimum levels of 67, 63, and 40 ppb Hg, respectively, in August. Starting in late August, content of mercury in organic surface horizons increased sharply to a maximum of about 133 ppb Hg in late September afterwhich levels declined towards summer values. Emanations of gaseous mercury, measured directly above litter and mineral soil horizons, were low or not detectable during most of the spring and summer but increased dramatically during August and September to a maximum of 4.9 ug Hg/m^2/day. The two to three fold increase in mercury levels in litter layers coincides with the large flux of gaseous mercury during the fall season. The release of gaseous mercury and the subsequent temporary enrichment of mercury in organic soil

horizons appears related to seasonal trends in soil moisture and temperature.

Return of atmospheric mercury to soil through dry deposition and rainfall occurred at levels and rates below the detection limit of the method. Results of the pyrolysis experiment suggested that the surface soil horizons contained a variety of mercury compounds and/or a diversity of ways in which mercury is organically bound. Negative enrichment of mercury does not accompany decomposition of leaves in the field.

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I. INTRODUCTION

Strong interest in mercury in the environment stemmed from both the Minamata (1956) and Niigata (1965) catastrophies where acute toxic effects were observed in people consuming contaminated fish. The source of mercury contamination was traced to certain industrial wastes. Following investigations of these incidents, interest in the distribution of mercury spread to other areas and mercury was found to be widely dispersed.

Mercury is naturally present in the environment however, the concentration usually ranges from a few parts per billion to a few hundred parts per billion (Shacklette *et al.*, 1971; McKeague and Kloosterman, 1974). Mercury is readily cycled in nature. Through biological and chemical processes, pathways exist for the movement of mercury in the environment. Mercury is present in rocks, soils, plants, water, and air and is continuously cycled among components of the terrestial and aquatic ecosystems.

A few recent studies have shown that organic layers of Luvisolic soils contain elevated levels of mercury in comparison to levels of mercury in underlying mineral soil horizons and in grassland soils (John *et al.*, 1975, McKeague and Kloosterman, 1974, Dudas and Pawluk 1976). Samples of leaf litter from forested soils in Alberta appear to contain 5 to 20 times as much mercury as that in most mineral soils in the prairie regions of Western Canada (Dudas and Pawluk, 1976). Reasons remain to be documented for such elevated

levels.

Several accumulative mechanisms have been described in the literature in an attempt to explain abnormally high levels of mercury in certain soils (Jonasson, 1970). These mechanisms may also account for the apparently elevated levels of mercury in LFH horizons of forested soils. First, mercury in the rooting zone may be taken up by the macroflora, translocated in the plant and then returned to the soil surface by deposition of leaves and needles. With decomposition of these plant residues, mercury may become negatively enriched. Secondly, mercury in a vaporous form emanating from the earth's crust and mantle may diffuse upward through mineral horizons and become adsorbed on humic material in the organic rich layers. Thirdly, mercury in the atmosphere may be adsorbed by the flora and by the organic layer itself. Precipitation may enhance the transfer of atmospheric mercury to soil.

Little is known about how these mechanisms collectively contribute to the mercury status of Luvisolic soils or of soils in general. Indeed, almost all previous studies on soil mercury have simply dealt with static measurements of the total quantity of mercury in order to obtain a background level. Studies have not been conducted to evaluate the possible fluctuations in normal background levels of mercury in a given soil during the seasons despite the fact that mercury is notorious for its mobility particularly in biologically enriched environments and is

continually lost from and added to soil in response to global cycling of the element. Elevated levels, such as those reported for the Luvisolic soils, may be transient and a reflection of conditions where the rate of addition of mercury temporarily exceeds the rate of loss of the element.

Accordingly, the objective of this study was to characterize and illustrate the dynamic behavior of mercury in soil through quantitative and qualitative assessment of seasonal fluxes and balance of mercury associated with surface horizons of deciduous forested soils. A motivating assumption at the onset of the study was that levels of mercury in soil vary seasonally in some systematic but as yet, unidentified manner. To achieve the objective continuous and intermittent measurements were made to quantify levels of mercury in forest vegetation, in rainfall, in soil gases, and in dry deposition during various times of the year as a measure of imputs. Potential loss and/or negative enrichment was assessed by monitoring levels of mercury in fresh litter as it decomposed under field and laboratory conditions. Levels of mercury in L, F, H, and Ah horizons were continuously measured for two years to ascertain the seasonal fluctuations and net balance.

II. LITERATURE REVIEW

Mercury is widely distributed throughout the environment. This element is present in the lithosphere, biosphere, atmosphere, and hydrosphere in various chemical and physical forms. There is a constant global cycling of natural and anthropogenic sources of mercury through these four environmental reservoirs in response to a combination of biological, chemical, and physical processes. Because mercury is cycled through the four reservoirs, it obviously must move through the soil. Therefore, soils are subject to inputs and outputs of mercury.

These inputs and outputs of mercury to and from the soil depend on geological, biological, and atmospheric contributions to the global cycle of mercury. The aim of this literature review is to bring together the details on geological, biological, and atmospheric contributions to the mercury status of soils. The contributions to the mercury cycle refer to tranfers, losses, and additions of mercury.

A. Global Cycle of Mercury

Element cycling models are often used to describe dispersion of materials on a global basis and to estimate the change of the natural chemical cycle due to man's activities. The global mercury cycle describes the fluxes of mercury among the earth's atmosphere, land, rivers and streams, oceans, and sediments.

Estimates of pre-man and present cycles of mercury are shown in Figures 1 and 2 taken from Garrels et al., (1973). The model of pre-man cycle of mercury (Figure 1) depicts four major reservoirs which includes the earth's atmosphere, land, oceans, and sediments. The pre-man cycle of mercury is considered to represent a steady state condition (Garrels *et al.*, 1973) therefore , there is no net accumulation or net removal of the element in each of the reservoirs.

The estimate of the flux of mercury to the oceans from weathering of rocks is considered to be equal to its depositional rate to the reservoir (1.3 X 10^9 g Hg/year) (Garrels *et al.*, 1973). The rate of mercury transport from uplift and erosion from sediments to land is also considered to be equal to the depositional rate of mercury.

The amount of mercury released to the atmosphere from land and sea surfaces is assumed to be equal to the amount of mercury vapor rained out of the atmosphere to the land and sea surfaces (Garrels *et al.*, 1973). The total mercury flux to the earth's surface was computed to be 2.5 X 10^{10} g Hg/year, and the mercury fallout on land and sea surfaces is proportional to their surface areas.

The mercury masses in oceans, land atmosphere, and sediments are 4.15 X 10^{13}, 1.0 X 10^{13}, 4.0 X 10^9, and 3.3 X 10^{17} g Hg, respectively. The mercury mass in land was determined by using total land area less that covered by ice (1.33 X 10^{18} cm^2), average soil thickness (60 cm), soil density (2.5 g/cm^3), and mean content of mercury in soil (50

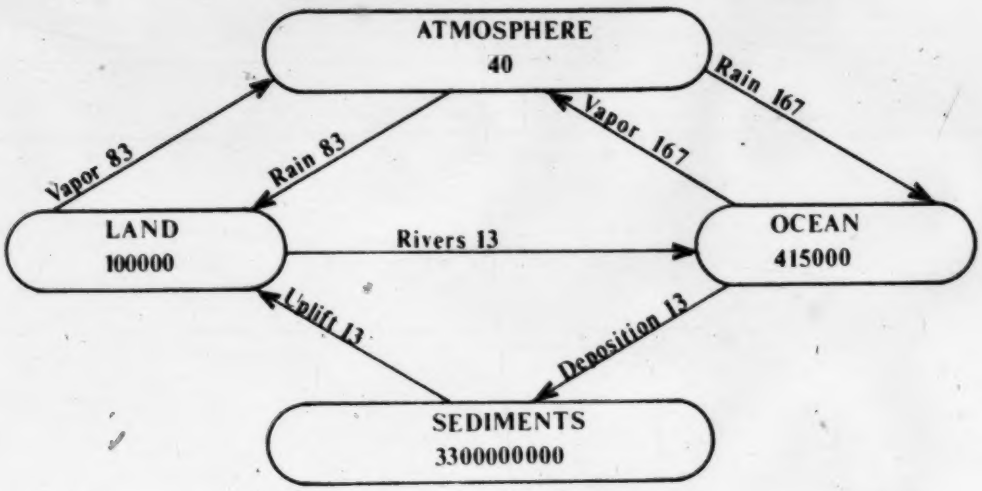

Figure 1. Model of pre-man cycle of mercury. Reservoir masses in units of 10^8 g; fluxes in units of 10^8 g/yr (taken after Garrels et al., 1973).

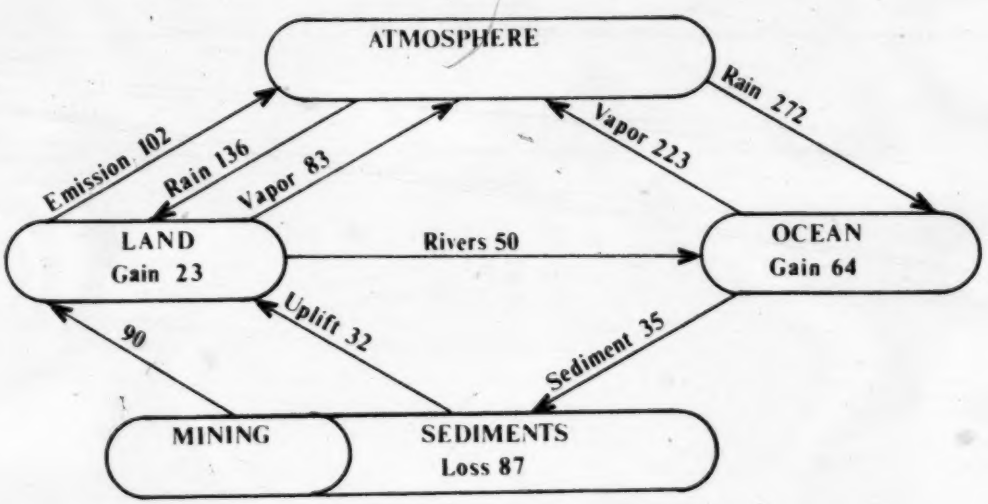

Figure 2. Model of present-day cycle of mercury. Reservoir masses in units of 10^8 g; fluxes in units of 10^8 g/yr (taken after Garrels et al., 1973).

ppb). The value of soil density (2.5 g/cm^3) used by Garrels et al., (1973) is particle density and not bulk density which should have been used in the calculation. If bulk density had been used, the value of mercury mass in land would have been 50% lower.

The mean residence times of mercury in the four reservoirs are 11 days for the atmosphere, 3200 years for oceans, 2.5 X 10^8 years for sediments, and 1000 years for the land mass (D'Itri *et al.*, 1972). A short mean residence time is paralleled by a small concentration of mercury, whereas a build up of mercury occurs in the reservoirs where the mean residence time is large. The relatively short mean residence time of mercury in the atmosphere demonstrates the high chemical and biological reactivity of elemental and organo-mercurial compounds. Mercury released to the atmosphere by vaporization of elemental mercury and its compounds is in a highly reactive form, widely distributed and quickly returns to the earth's surface. The relatively long mean residence time of mercury in sediments, oceans, and land demonstrates that, as mercury is released from the weathering of rocks, it becomes chiefly water-transported in a relatively unreactive form. This mercury then becomes buried in sediments, where it remains relatively unreactive. A large amount of mercury is fixed in sediments and rocks but with weathering, a small amount is mobilized and quickly cycled through the atmosphere, land, and oceans.

The model of the present-day cycle of mercury (Figure 2) depicts the anthropogenic sources of mercury, and its effect on the four major reservoirs. The model of pre-man cycle of mercury serves as background for the model of present-day mercury cycle. The main differences between the two models are the higher fluxes between reservoirs of the present-day mercury cycle as compared to the pre-man cycle.

Anthropogenic sources of mercury cause levels to rise in air, soil, freshwater lakes and streams, and ocean estuaries (D'Itri *et al.*, 1972). Some of the anthropogenic sources include mining, chlor-alkali production, combustion of fossil fuels, cement manufacturing, and roasting of sulfide ores (Fimreite, 1970).

Unlike the pre-man mercury cycle, the present-day mercury cycle is not in a steady state condition because the land and ocean reservoirs have a net gain of mercury, while the sedimentary rock reservoir has a net loss of mercury. The atmospheric reservoir remains in a steady state condition.

In the present day cycle the fluxes of mercury from oceans to sediments, from sediments to land, from land to oceans, and from land to the atmosphere are 3.5 X 10^9, 3.2 X 10^9, 5.0 X 10^9, 1.02 X 10^{10} g Hg/year, respectively. There is also a flux of 9.0 X 10^9 g Hg/year to the land reservoir due to mining.

The present total flux of mercury to the atmosphere from land and sea surfaces is 4.08 X 10^{10} g Hg/year. As in

the pre-man cycle, the input of mercury to the atmosphere from the land and sea surfaces is assumed to be equal to the amount of mercury vapor rained out of the atmosphere. Its distribution upon return to the earth's surface is in proportion to the land and sea surfaces. There is a net increase of 2.3 X 10' g Hg/year to the land surface because of the net results of mining and utilization of mercury on land, and the increased mercury content of rain over land.

Several conclusions can be made through the use of mercury cycling models. The atmosphere plays an important role in the mobilization of mercury. The flux of mercury from the earth's surface to the atmosphere is several times larger than that occurring between continents and oceans. The use of mercury by man and the subsequent emissions to lands, rivers, and lakes, together with increased erosion rates have elevated mercury contents of lakes and rivers by a factor of two to four. Increases in total content of mercury in oceans has been negligible. The content of mercury in soils appears to have increased only by 0.02%.

The small increase in content of mercury in soils from pre-man levels suggests that the addition of anthropogenic sources of mercury does not cause an appreciable net accumulation of mercury in the land reservoir. It also suggests mercury in soil is highly dynamic like water, carbon, and nitrogen. The increased amount of mercury entering the land and soil segment of the present-day mercury cycle is lost to the earth's atmosphere, rivers and

streams, oceans, and sediments.

B. Contributions to the Mercury Cycle and to the Mercury Status of Soils

In this section of the literature review, emphasis will be on the land and soil segment of the global natural mercury cycle. In view of the preceeding discussion dealing with the cycling of mercury, and with some hindsight, it is apparent that the mercury status of soil is only partially determined by the initial geologically inherited mercury levels (content of mercury in soil parent material). The mercury status of soil is also influenced by the nature and magnitude of transfers, losses, and additions of the element during soil evolution. Transfers, losses, and additions of mercury occurs in response to the large scale geological, biological, and atmospheric contributions to the cycling of mercury. The movement of mercury into and from the soil appears related to volatilization and transfer of mercury through the soil to the atmosphere largely through geologically related phenomenon, return of mercury to the land mass and soil by precipitation and adsorption, vegetative cycling of mercury through soil, and loss of mercury back to the atmosphere through biological and physical-chemical reactions.

Terrestial abundance of mercury

The abundance of mercury in the earth's crust is 80 ppb (Krauskopf, 1967). The average content of mercury in both

granite and basalt is 80 ppb Hg while shale contains an average of 400 ppb Hg. Sandstone and limestone each contain an average of 75 ppb mercury (Garrels *et al.*, 1973). These rock types constitute, alone or in combination, the source of geologically inherited mercury in the parent materials of most soil. Accordingly, one could expect that the initial amount of mercury associated with mineral materials in soils would be, in general, about 80 to 100 ppb. On this basis, most soils appear to have experienced a net loss of mercury. For example, the mean geometric concentration of 912 soil samples collected and analyzed from numerous sites throughout the United States was 71 ppb Hg (Shacklette *et al.*, 1971). The average content of mercury in 253 samples collected from various locations throughout Canada is 54 ppb (McKeague and Kloosterman, 1974). The lower contents of mercury in soil compared to its geochemical abundance reflects the dynamic nature of soil mercury and loss of the element from soil mineral components.

Volatilization and transfer of mercury to the atmosphere

Mercury is a naturally occurring element and because of the high volatility of elemental mercury and some of its organic compounds, it is widely dispersed in the earth's atmosphere. Release of mercury to the atmosphere can occur through weathering of rock, volcanic emissions, biological emanations, and degassing of the earth's mantle and soil.

Estimates of the amount of mercury released from these processes varies greatly. The weathering of rock has been

estimated to release 230 tons mercury per year (Joensuu, 1971) and 5000 tons mercury per year (Goldberg, 1970).

A paucity of information existed on the release of mercury through volcanic processes until the recent study published by Siegel and Siegel (1978) on mercury emissions associated with the Kalalua eruption in Hawaii in 1977. Preeruptive values of 1 ug Hg/m^3 were found, while during the beginning of full scale volcanic activity mercury emissions were 50 to 200 ug/m^3. Measurements of mercury released to the atmosphere from Sulfur Banks, a fumarole in Hawaii, were also made by Siegel and Siegel (1978). Measurements made at ten meters from emission sites showed the level of mercury released to the atmosphere was 800 $ug/m^3/day$. At stations 200 and 380 Km away from the fumarole, the level of mercury in the atmosphere was 1/10 as much. Mercury released from point sources such as volcanoes and fumaroles can increase the atmospheric levels, however, the magnitude of such contributions are not accurately documented.

Degassing of the earth's crust, a major process in the mobilization of mercury from land masses, has been estimated to range from 25 to 150 X 10^3 tons of mercury per year (Weiss *et al.*, 1971). Degassing rates measured in California by various authors range from 0.0014 to 10 ug $Hg/m^2/day$ (D'Itri *et al.*, 1972). The higher rates of degassing typically occur over mineralized areas while the lower rates are encountered over non-mineralized areas. Calculations

based on a state by state inventory of mercury emanations from mineralized and non-mineralized areas indicate the average degassing rate for the United States is 1.3 X 10 ^{4} g Hg/m^2/year (Van Horn, 1975). This degassing rate is equivalent to 0.36 ug/m^2/day. The amount of mercury present in a square meter of soil, to a depth of 50 cm, that had a bulk density of 1.2 g/cm^3 and a concentration of mercury of 70 ppb would be 42,000 ug Hg. Assuming the degassing rate is 0.36 ug/m^2/day it would take 320 years for as much mercury to move through soil from degassing as total mercury present in the soil. In Alberta, the two study areas of this project are not over mineralized areas and a low degassing rate (less than 0.36 ug/m^2/day) would be expected.

Mobilization of mercury is also attributable to biological processes. Bacteria have been found to volatilize methylmercury aerobically as well as anaerobically (Spangler *et al.*, 1973; Magos *et al.*, 1964). Several methane-producing species of bacteria are known to degrade methylmercury producing methane as a degradation product along with inorganic mercury as Hg^{+2} (Spangler *et al.*, 1973). The mercuric ion can be reduced to mercury metal which vaporizes and dessiminates through the atmosphere. Bacteria of the genus *Pseudomonas* can preform the reduction of divalent inorganic mercury to elemental mercury (Magos et al. 1964; Furukawa *et al.*, 1969). The production of elemental mercury through biologically mediated reactions could be important in the eventual volatilization of mercury from soil.

These geological, biological, and other purely chemical processes account for the mobilization of mercury to the atmosphere. The annual natural flux of mercury to the atmosphere is from 25,000 to 30,000 metric tons per year (Korringa and Hagel, 1974; Heindryckx *et al.*, 1974; Wollast *et al.*, 1975). Estimates of natural and anthropogenic sources of mercury released to the atmosphere collectively range from 41,000 to 50,000 metric tons. Opinions on the relative magnitude of natural and anthropogenic sources of mercury released to the atmosphere differ in the literature. Some authors state man and nature contibute equally to the total amount of mercury released to the atmosphere (Lockertz, 1974; Goldberg, 1970). However, others feel anthropogenic sources of atmospheric mercury can not rival the degassing rate of the earth's mantle (Weiss *et al.*, 1971; Joensuu, 1971; Jernelov *et al.*, 1975; Korringa and Hagel, 1974; Heindryckx *et al.*, 1974; Wollast *et al.*, 1975; Boyle, 1971). Even though the natural output of mercury may exceed the anthropogenic output of mercury, man's activities have had an effect on the amount of mercury circulating in the environment (Figure 2).

Mercury does not appear to be uniformly distributed throughout the atmosphere. Over areas of non-mineralization content of mercury in the air is generally in the range of 1 to 10 ng/m^3 for the United States (Johnson and Braman, 1974; McCarthy *et al.*, 1970). A world average of 20 ng Hg/m^3 was estimated by Eriksson (1967) while Williston (1968)

suggested values ranged from 1 to 50 ng Hg/m³ with an average of 3 ng/m³ in the San Francisco Bay area. Caldwell (1972) reported atmospheric levels of mercury over non-mineralized land areas in the United States to be in the range of 1 to 200 ng Hg/m³. Over areas of mineralization, levels of mercury appear to be 10 to 1,000 times greater (Caldwell, 1972).

Williston (1968) reported levels of mercury in the air over the open sea were 0.6 to 0.7 ng Hg/m³. The low levels of mercury found in the air over the ocean suggests that the land surface is the principal source of atmospheric mercury. Atmospheric content of mercury above land masses appears to be higher than levels above oceans, even in areas which are free from obvious pollution. The heterogenous nature of atmospheric levels of mercury reflects the short mean residence time of the element in the atmosphere.

In addition to geographical differences, seasonal variations in the concentration of mercury in the atmosphere have been noted. For example, in the San Francisco Bay area the lowest values (0.5 to 25 ng Hg/m³)were found in winter while the highest values (1 to 50 ng Hg/M³) were found in the summer. The low values occurred when winds were predominantly from the oceans and the high values occurred when winds were mainly from the land.

Levels of mercury in the atmosphere are not uniform with altitude. Atmospheric concentrations of mercury in Tampa Bay, Florida varied with height above ground (Johnson

and Braman, 1974). Mercury levels at 0.1 meter were higher than levels at 10 meters above ground. At the Ord mine in Arizona, concentrations of mercury at ground surface vary from 108 to 20,000 ng/m³ to 24 to 108 ng/m³ at 400 feet (McCarthy *et al.*, 1970).

Conflicting information exists in the literature on the diurnal changes in the levels of atmospheric mercury. For example, levels of atmospheric mercury increased at night and decreased during the day over land in the Tampa Bay area (Johnson and Braman, 1974). The magnitude of the levels of atmospheric mercury were directly opposite to the air-temperature fluctuations. In contrast, the amount of mercury in the air at the Ord mine in Arizona reached maximum levels of mercury near midday and minimum levels at 2:00 a.m., a trend that parallels the diurnal change in the air-temperature (McCarthy *et al.*, 1970).

Only limited information exists on the form of mercury in the atmosphere. Studies on atmospheric speciation of mercury in Tampa Bay, Florida showed more than 90% of the mercury in the air was primarily "volatile" and composed of Hg-II type compounds, methylmercury-II type compounds, and elemental mercury (Johnson and Braman, 1974). "Particulate" mercury represented less than 10% of the total mercury in the air near the ground. The low level of "particulate" mercury in the air suggests that mercury accumulation on vegetation or soil surfaces from dry deposition would not be as important as other accumulative processes such as direct

adsorption.

Return of mercury to the landmass and soil by precipitation and adsorption

Mercury released to the atmosphere is rather quickly returned to the earth by deposition. Deposition can occur by both wet and dry processes. Deposition of mercury on the solid surface of the earth, estimated by Weiss et al (1971), is between 2.5 X 10^{10} g Hg/year (equivalent to more than 2 g Hg/ha/year) to 1.5 X 10^{11} g Hg/year. The amount deposited onto the soils of Sweden by rain is 1.2 g Hg/ha/year (Andersson and Wiklander, 1965). If 1.2 g Hg/ha/year of mercury is added to a soil with a bulk density of 1.20 g/cm^3 and to a depth of 2 cm, without volatilization losses of any of the mercury, the annual increase of mercury to the soil would be equivalent to 50 ppb. Since most soils generally contain 50 to 80 ppb Hg, there must be an annual turnover of mercury equivalent to the amount added via yearly precipitation.

One possible mechanism for the surface deposition of mercury from the atmosphere is the removal of mercury by condensation or adsorption on dust particles (Williston, 1968). If mercury is in the form of particulate matter, dry deposition rates would be proportional to aerosol levels (Matheson, 1977). Suspended particulate material was found to contain 50% of total mercury present in laboratory air, while settled dust contained lower levels of mercury suggesting that mercury is mainly associated with submicron

particles (Kothny, 1973). The large surface area of submicron particles for contact with mercury vapor could explain the large proportion of mercury associated with the small particles.

However, some studies suggest that mercury in particulate matter only makes up a small fraction of the total mercury content of the air. For example, in a study consisting of 54 speciation measurements in the Tampa Bay metropolitan area, mercury in the particulate form only represented 4% of the total mercury content of the air (Johnson and Braman, 1974). In air samples of Chicago air mercury in particulate form contained an average of 4 ng/m^3 while mercury in elemental form averaged 22 ng/m^3 (Wroblewski, 1974).

There also appears to be some discrepancy in the literature on the effectiveness of rainout and washout. For example, reported measurements showed a heavy rainstorm can completely washout mercury in the air even in polluted areas (McCarthy *et al.*, 1970) and McLean (1976) suggests that mercury concentrates in rainfall and snowfall. However, it has also been reported that the total mercury in the air was not affected before, during, and after a thunderstorm (Johnson and Braman, 1974) and that after a rainstorm the levels of mercury in the atmosphere increased (Cooper *et al.*, 1975).

The effectiveness of rain to remove mercury from the atmosphere depends on the solubility of mercury in water.

Mercury in the vapor phase has a higher solubility in distilled water saturated with air (47 ug/liter) compared to deaerated water under nitrogen (20 to 30 ug/liter) (Kothny, 1973). It is possible that levels of mercury in the atmosphere could be affected by whether a cold or warm front produced the rainstorm. Cold fronts provide and circulate fresh air (as compared to a warm front) and the level of merrcury in the atmosphere may decrease during the rainstorm, while during a warm front the level of mercury is not affected or is even increased by the rainfall (Kothny, 1973). The solubility of mercury vapor is known to increase with increased acidity (Lockeretz, 1974) which suggests acid precipitation could be an effective medium for the washout of atmospheric mercury.

The effectiveness of wet and dry deposition of atmospheric particulate matter containing mercury appears to be uncertain. However, deposition of mercury vapor (vapor impact) occurs. Dry mercury vapor is adsorbed by organic materials in soil which are strong adsorbers of mercury vapor from the air (Matheson, 1977) and by aerial surfaces of plants (Siegel *et al.*, 1974; Lindberg *et al.*, 1979; Huckabee and Janzen, 1975). Dry mercury vapor impact also occurs onto water surfaces (Ontario Ministry of the Environment, Air Resources Branch, 1978).

Recent findings in a study of atmospheric mercury deposition in Ontario showed that the mercury flux associated with precipitation was 30 ug/m^2/year at

Mississauga and 20 ug/m²/year at Dorset. Particulate mercury deposition rates were 5 ug/m²/year in Mississauga and essentially non-detectable at Dorset; constituting a small fraction of the total mercury deposition flux (Shroeder, 1981). Dry vapor deposition rates were estimated by mass transfer coefficient calculations to range from 45 to 110 ug/m²/year. However, even though dry vapor deposition appears to be the major contributor to the total mercury flux and compared to dry particulate deposition and precipitation, it is at present the least precise measured component.

The role of vegetation

Since mercury is not totally excluded during the process of ion uptake by plants, the element is biocycled through soils. Most terrestial plants, excluding those treated with mercury-containing pesticides, do not contain high levels of mercury (Lagerwerff, 1972), Usually, levels of mercury in plant tissue are substantially lower than levels in soil upon which the plants grew even in regions where soils contain naturally elevated amounts of mercury (Shacklette *et al.*, 1970). Although most mercury in plant tissue arises from uptake of the element from soil, a small amount of atmospheric mercury is adsorbed onto aerial plant surfaces (Siegel *et al.*, 1974; Lindberg *et al.*, 1979; Huckabee and Janzen, 1975).

In contrast to higher plant forms, mosses, lichens, and basidiomycetes act as accumulators of mercury. Levels of

mercury in mosses and lichens were enriched from six to eight fold compared to amounts in soil (Siegel and Siegel, 1973). These authors also report basidiomycetes, the major litter and wood decomposing organisms in forested soils, contain 3.5 times as much mercury as in the host soil. Since mercury in these lower plant forms originates from the supportive media (soil) the organisms, upon death, do not create a new input of mercury. Instead, their contribution would be in retarding the volatilization and loss of soil mercury. Soil dwelling organisms that accumulate mercury would also increase the mean residence time of the element which in turn determines the total quantity present in soil.

Mobilization of soil mercury

Mercury is released from the soil back to the atmosphere through several reactions. One common process involves the reduction of the mercuric ion to volatile metallic mercury (Jernelov, 1972). Bivalent mercury can be converted biologically to the volatile forms of monomethyl or dimethyl mercury (Jernelov, 1972).

The role of microorganisms in mobilizing mercury from soil was clearly demonstrated by Landa (1978). In his experiments, samples of soils were either left untreated, autoclaved, or incorporated with glucose. The treatments were designed to suppress and to stimulate microbial activity. Soil samples were then ammended to 1 ug Hg/g soil, incubated, and the loss of mercury from each treatment was monitored over time. Autoclaving greatly suppressed the loss

of mercury from soil compared to the losses incurred when glucose was added to stimulate biological activity. In 10 days, glucose treated samples had lost 5 to 35% of the added mercury depending on the soil sample while in the same time interval, autoclaved samples only lost 1 to 10% of the added mercury. The increased mercury loss rate accompanying glucose additions and the suppression of losses with autoclaving clearly demonstrate soil biota plays a major role in the mobilization of mercury from soils.

A similar conclusion concerning the role of microorganisms was suggested in a study of the nature of mercury in Chernozemic and Luvisolic soils in Alberta. Dudas and Pawluk (1976) found that in Chernozemic soils, lowest values of mercury were always found in biologically enriched horizons. For Chernozemic soils, Ah horizons contained an average of 26 ppb Hg while respective C horizons contained an average of 44 ppb Hg. These authors concluded that the lower content of total mercury in A horizons as compared to levels in C horizons, was due to the volatile loss of mercury promoted by microbial activity.

In another study, samples of Ap horizons from cultivated Solonetzic, Chernozemic, Luvosolic, and Gleysolic soils in Alberta were shown to contain from 20 to 40 ppb Hg (Dudas and Pawluk, 1977). These cultivated soils were known to have received mercury from pesticide chemicals. In 1976 these authors showed that uncultivated Chernozemic soils, presumably free of mercury contamination, contained 20 to 35

ppb Hg. Since there was little difference between contents of mercury in cultivated soils and in virgin soils, the extensive use of pesticides containing mercury for cereal crop production in Alberta (Fimreite, 1970) did not result in permanently elevated levels of soil mercury. The added mercury must have volatilized through microbial activity.

It has also been shown that elemental mercury evolution is mediated by humic acid. This reaction, which is a reduction, envolves the interaction of the mercuric form with the free radical electrons of humic acid (Alberts *et al.*, 1974).

C. Mercury in Soil

Mercury is ubiquitous in the natural environment but its concentration usually only ranges from a few parts per billion to a few hundred parts per billion. The abundance of mercury in soil is usually similar to or somewhat less than crustal abundance (80 ppb).

Shacklette et al (1971) collected and analyzed 912 samples of soil from numerous sites throughout the United States and found the geometric mean concentration of mercury was 71 ppb. A mean value of 60 ppb Hg typifies the mercury status of several British soils (Warren and Delavault, 1969). In Alberta, Dudas and Pawluk (1976) found levels of mercury in uncultivated Chernozem soils averaged 26 ppb Hg for Ah horizons while C horizons from the same soils contained an average of 44 ppb Hg. Soil horizons from

Chernozems and Luvisols from both cultivated and uncultivated soils in Saskatchewan contained from 10 to 40 ppb Hg with none of the horizons exceeding 60 ppb Hg (Gracey and Stewart, 1974). It is not apparent why contents of mercury in Canadian soils are substantially lower than levels in soils in the United States.

Some soils contain levels of mercury that are much higher than the aforementioned average values. Soils with elevated levels of mercury are often located over deposits of cinnabar or polymetallic ores (Jonasson and Boyle, 1972; John *et al.*, 1975; Fedorchuk, 1958), in regions of volcanic activity (Sigel and Siegel, 1978), and in regions where tectonic disturbances prevail (Jonasson and Boyle, 1972). Because of its high vapor pressue, gaseous mercury can escape from hydrothermal solutions (Fedorchuk, 1958). The vaporous mercury can then penetrate host rocks, where it may be deposited as cinnabar or as a finely dispersed elemental mercury. Gaseous mercury is readily intercepted by bituminous carbonaceous clay shales (Fedorchuk, 1958). Some shales and coal deposits may contain an appreciable amount of mercury and could account for higher levels of mercury in some soils (Hammond, 1971; Fedorchuk, 1958).

Soils located in a general mercuriferous belt in British Columbia contain relatively high concentrations of mercury (John *et al.*, 1975). The average content of mercury in the surface mineral horizons was 85 ppb Hg. In Pinchi Lake, British Columbia, an area of cinnabar deposits,

background levels of mercury in soils range from 10 to 310 ppb Hg (John *et al.*, 1975). Some soils in Britain were found to contain 0.25 to 15 ppm Hg (Warren *et al.*, 1969). These soils were close to the Gotrum Mine in Erie where significant amounts of mercury occur as a by product of base metal refining.

Elevated levels of mercury often occur in soil horizons enriched in organic matter (Shacklette *et al.*, 1971; John *et al.*, 1975). In British Columbia the surface horizons of peaty muck soils and those predominated by vegetative litter contained an average of 164 ppb Hg (John *et al.*, 1975). Elevated levels of mercury present in soil horizons enriched in organic matter were also observed by Dudas and Pawluk (1976) in a study of Luvisolic soils in Alberta. They found levels of mercury in forest litter were several times higher than amounts in underlying mineral horizons. The levels of mercury in surface horizons of Luvisolic soils ranged from 79 to 155 ppb Hg. Levels of mercury in the range of 81 to 186 ppb were reported in forest litter samples from several other Canadian locations (McKeague and Kloosterman, 1974). High humus content is a requisite for contents of mercury to exceed 150 ppb in uncontaminated soils (Andersson, 1967), however, high levels of soil mercury are not always significantly correlated with content of organic matter.

To highlight the dynamic nature of mercury in soil, one further study, by Jones and Hinesly (1972) will be presented. These authors analyzed soil samples which were

collected over a 63 year period from the Morrow soil test plots at the University of Illinois for total mercury. The following contents of mercury in surface soil samples and respective sampling year were reported by the authors: 0.41 ppm Hg in 1904 samples, 1.1 ppm Hg in 1913 samples, 0.82 ppm Hg in 1923 samples, 0.34 ppm Hg in 1933 samples, 0.09 ppm Hg in1944 samples, 0.15 ppm Hg in 1955 samples, and 0.07 ppm Hg in 1967 samples. The sampled plots were located in poorly drained positions but in 1904 a tile drainage system was installed. The initial rise in amount of mercury following installation of the tile drainage system was attributed to the effects of improved aeration. With improved aeration at depth, mercury compounds previously stable under anaerobic conditions were thought to be converted to volatile vaporous forms. Organic matter and newly formed iron and manganese oxides in surface soil layers effectively trapped upward diffusing vaporous mercury accounting for the elevated levels in samples collected in 1913 and 1923. Subsequent to 1923, levels gradually declined as surface adsorbed mercury was gradually mobilized to the atmosphere eventually reaching a level (0.07 ppm) in 1967 commensurate with the geochemical abundance of mercury.

III. MATERIALS AND METHODS

Two study areas, one at the Ellerslie Research Station and one east of Sherwood Park, in the Cooking Lake moraine, were selected to conduct experimental research designed to evaluate gains, losses, and seasonal balance of mercury associated with the litter layer of deciduous forested soils.

The climate of the two study areas is similar and is characterized by relatively warm summers and cold winters with a subhumid moisture regime. The mean summer temperature (May to September) is 13°C and the mean winter temperature (November to March) is -9°C. Winter temperatures rarely fall below -40°C, and summer highs rarely rise above 32°C. The average frost free period is 100 days. The mean annual precipitation is between 40.6 and 45.7 cm for the entire Edmonton sheet 83-H (Bowser *et al.*, 1962). The annual precipitation for the Ellerslie study area for the years 1977, 1978, and 1979 were 42.3 cm, 41.8 cm, and 39.1 cm respectively (data from Ellerslie Meteorological Station records). There was no precipitation data available for the Cooking Lake study area. The wind velocities average less than 16 km/hour and the dominant wind direction is from the northwest (Bowser *et al.*, 1962).

The Ellerslie study area was located in NW-24-51-25 W4 and consisted of a sampling area of about 0.5 hectares. Soils in this study area are developed on lacustrine parent material with native vegetation still present. The

topograghy of the area is gently undulating. The dominant soils in the study area consist of Eluviated Black Chernozems in upper slope positions and Humic Gleysols in the depressional sites. Morphological characteristics of the soil most frequently encountered (Orthic Humic Gleysol) during sampling within the 0.5 hectare area are described in Table 1.

In 1979, soil temperatures at 100 cm depth at the Ellerslie study area peaked in July with an average monthly soil temperature of 8°C. In August and September of 1979, soil temperatures at 100 cm averaged 7°C for the two months. Soil temperatures at the 20 cm depth peaked in July in 1979 at an average monthly value of 12°C. In 1978, soil temperatures at the 100 cm depth, reached a maximum in August averaging 11.5°C and peaked at the 20 cm depth in July at 14.4°C (data from Ellerslie Meteorological Station records).

Vegetation at the Ellerslie study area consisted predominantly of *Populus balsamifera* (Balsam poplar) and *Populus temuloides* (Aspen poplar). Understory vegetation included *Rosa woodsi* (wild rose), *Cornus stolonifera* (dogwood), *Viburnum trilobum* (high bush-cranberry), *Symphoricarpus albus* (snowberry), *Prunus virginiana* (chokecherry), *Rubus strigosus* (raspberry), and *Linnaea borealis* (twinflower).

The locations of the sampling areas east of Sherwood Park in the Cooking Lake moraine area are SE-5-53-21 W4,

Table 1. Morphological description of the soil at the Ellerslie study area.

Classification: Orthic Humic Gleysol

Location: NW-24-51-25 W4

Parent Material: Lacustrine

Landform: Lake plain

Vegetation: *Populus balsamifera, Populus tremuloides, Rosa woodsii, Cornus stolonifera, Viburnum trilobum, Symphoricarpos albus, Prunus virginiana, Rubus strigosus, Linnea borealis*

Horizon	Depth (cm)	Description
L-H	13-0	Black (10YR 2/1, m) semidecomposed organic matter; fibrous plentiful, coarse and medium, random roots; abrupt smooth boundary; 11 to 15 cm thick; pH 6.5
Ahg	0-10	Black (10YR 1.7/1, m) loam; moderate fine granular; friable; plentiful fine and medium oblique exped roots; clear smooth boundary; 7 to 12 cm thick; pH 6.0
Aejg	10-18	Brownish black (2.5Y 3/2, m) loam to silt loam; weak, fine platy; friable; few fine and medium oblique exped roots; gradual smooth boundry; 5 to 10 cm thick; pH 5.7
Btjg	18-67	Olive brown (2.5Y 4/3, m) clay loam; moderate fine subangular blocky; firm; gradual smooth boundary; 46 to 55 cm thick; pH 7.4
Ckg	67+	Olive brown (2.5Y 4/3, m) clay loam; massive; slightly plastic; pH 7.4

NE-35-52-21 W4, NW-33-52-21 W4, and NE-33-52-21 W4. Areas used for sample collection at these locations each were about 0.5 hectares. At all four locations, the landform consisted of hummocky moraine associated with gently rolling and rolling topograghy . All soils were developed on till; those in the well-drained topograghic positions were classified as Orthic Gray Luvisols. All sample collection sites were located in upper slope positions. The morphological features of a typical pedon and the one sampled for characterization of total mercury is given in Table 2.

The dominant vegetation at the four sampling locations was *Populus tremuloides* (aspen poplar) with a minor component of *Populus balsamifera* (balsam polar) in many of the lower slope positions. Understory growth included *Rosa woodsii* (wild rose), *Cornus canadensis* (bunchberry), *Actae rubra* (baneberry), and *Corylus cornuta* (hazel). At each specific sampling site, aspen poplar was either the sole or dominant tree species present.

In order to monitor the mercury levels in surface soil horizons throughout the year samples of L, F, H, and Ah horizons were collected (Ah samples only from the Ellerslie site) in quadruplicate every two weeks at each study area throughout the years of 1977 and 1978. This frequent, almost continuous, sampling was done to ascertain possible fluctations in content of mercury and its balance over the two years. Leaf samples from trees and understory growth

Table 2. Morphological description of the soil at the Cooking Lake moraine area.

Classification: Orthic Grey Luvisol

Location: NW-33-52-21-W4

Parent material: Glacial till

Land form: Hummocky moraine

Vegatation: *Populus tremuloides, Populus balsamifera, Rosa woodsii, Cornus canadensis, Actae rubra, Corylus cornuta.*

Horizon	Depth (cm)	Description
L-H	6-0	Black (10YR 2/1, m) semidecomposed organic matter; fibrous, abundant coarse and medium random roots; abrupt smooth boundary, 4 to 7 cm thick; pH 6.4
Ae	0-6	Dull yellowish brown (10YR 5/3, m) loam to silt loam; moderate, fine platy; friable; few fine and medium oblique inped roots; abrupt smooth boundary; 4 to 7 cm thick; pH 6,5
AB	6-28	Dull yellowish brown (10YR 5/4, m) clay to clay loam; moderate, fine blocky; firm; few fine and medium oblique exped roots; clear smooth boundary; 18 to 24 cm thick; pH 6.0
Bt1	28-53	Dull yellowish brown (10YR 4/3, m) clay; strong fine subangular blocky; firm; gradual smooth boundary; 22 to 26 cm thick; pH 5.5
Bt2	53-70	Dull yellowish brown(10YR 4/3, m) clay; moderate fine subangular blocky; firm; gradual smooth boundary; 15 to 19 cm thick; pH 6.3
Ck	70+	Brownish black (2.5YR 3/2, m) clay loam; amorphous to weak coarse blocky; slightly plastic; pH 7.3

were collected periodically during the growing season and analyzed for total mercury in order to ascertain the possible translocation of mercury from the rooting zone through the plant and then back to the soil surface through the deposition of leaves.

Initially, the high levels of mercury reported in the literature for surface horizons of forested soils was thought to be due to the negative enrichment accompanying microbial decomposition of leaf fall. Accordingly, the extent of negative enrichment of mercury resulting from weight loss accompanying leaf litter decomposition was examined through two leaf decomposition experiments. Freshly fallen leaves were collected from the ground surface from both study areas in September of 1977 then stored in plastic bags in a large freezer at -10°C until the following spring. One decomposition study was conducted in the laboratory to preclude input or gain of mercury through rainfall or aerosolic accretion. The other study involved decomposition in the field under natural conditions. In the laboratory decomposition experiment, for each of the two sources of leaf material, two triplicate portions of moist leaves of about 100 g each were placed in large aluminum trays. To one triplicate set of samples, 10 mg N (as NH_4NO_3) was added with the first watering to promote an initial burst of microbial activity. The other triplicate set was not treated with nitrogen and served as a control. Distilled water, free of mercury, was added to all samples at weekly intervals or

as required to maintain samples moist. Trays were loosely covered with thin sheets of clear plastic and stored at normal room temperature. During the initial stages of decomposition, small subsamples were collected from the trays every two weeks and analyzed for mercury, organic carbon, and total nitrogen. Once the samples reached an advanced stage of decomposition, little sample remained consequently subsamples were taken on a monthly basis in order to extend the decomposition time.

In the field decompostion trials, triplicate 1 m^2 sites were cleared of previous litter material to expose mineral A horizons at each of the two study areas. To each site, about 15 cm of lightly packed leaf material, collected the previous fall from approximately the same location, was placed on the exposed mineral soil. All sites were located within a canopy of poplar; sites at the Cooking Lake study area were located on well-drained positions while those at Ellerslie were located on imperfectly-drained positions. Subsamples were collected from each triplicate site from the two forested areas biweekly, air-dried in the laboratory and then analyzed for content of mercury, organic carbon, and total nitrogen.

Mercury in soil gases was determined using the copper foil method of Siegel and Siegel (1978). Gaseous mercury emanations from the soil were measured at the Ellerslie study area in 1978 and at both study areas in 1979 by the copper foil technique. For the determinations, 2 mil thick,

high purity copper foil was cut into 5 cm^2 pieces. Prior to placement in the field the copper foil pieces were washed in 0.1 N HCl and then rinsed with 95% ethyl alcohol. Each piece of copper foil was then attached to the inside of a 100 mm diameter glass Petri dish. Placement in the field involved setting the petri dishes on the ground surface in a inverted fashion so the the foil faced downward. In this manner, the copper foil was shielded from the effects of wind, rainfall, and particulate matter which would come into contact with unprotected copper foil. Copper foil vapor traps were placed in triplicate above each of the L, F, H, and Ah horizons at Ellerslie and above each of the L, F, H, and Ae horizons at the Cooking Lake study area by removing apppropiate horizons that were not needed and placing the copper foil directly above the horizon being studied. Horizon material that was removed was not replaced as a cover over the inverted petri dishes. For each horizon being studied, the triplicate set of traps were distributed within an area of 0.5 m^2 and adjacent to sites used for the leaf decomposition trials. The copper foil vapor traps were collected every 8 to 10 days and analyzed for total mercury by complete digestion of the copper foil in nitric acid. This kind of mercury trap is claimed to be suitable for the collection of all forms of mercury (Siegel and Siegel, 1978).

Raingauges were placed in various locations throughout the Ellerslie study area during the summer of 1978 in order to measure the possible input of mercury from precipitation.

Event sampling was conducted and rain samples were analyzed for total mercury. Five raingauges spaced at approximately 3 m intervals were placed under the canopy of trees in order to collect canopy drip. Five other raingauges also spaced at 3 m intervals were placed outside the canopy in an open field immediately adjacent to the forested area. Open field rain samples were used to evaluate possible adsorption of mercury on live vegetation when rainwater was intercepted by the leaves of trees. After the first attempt in collection and analysis of water samples, it was found that spiked mercury was quickly lost from the collected open field rainwater and canopy drip. Addition of 500 mg $K_2S_2O_8$, in crystal form, to each collection device eliminated the loss of known mercury spikes, consequently, the oxidizing agent was added regularly to each collection container.

Soil samples collected from the study areas were air-dried in the laboratory; organic samples were ground with a Wyllie-mill and mineral samples were ground with a mortar and pestle. A portion of the ground sample was analyzed immediately for mercury. The rest of the sample was stored in air-tight glass jars for subsequent determinations.

Total nitrogen of the organic and mineral soil samples was determined by the semi-micro Kjeldahl method without precautions to include measurement of NO_3^- and NO_2^- (Manual of Soil Sampling and Methods of Analysis, 1976). Total carbon content was determined by the wet oxidation method of

Walkley-Black (Manual of Soil Sampling and Methods of Analysis, 1976). Ferroin indicator was used for the titration.

Content of total mercury was determined by a flameless atomic absorption method. Depending on the anticipated content of mercury, from 0.5 t0 2.0 g of sample was digested for 3 hours at 80°C using nitric acid and saturated potassium persulfate solution as described by Melton et al (1971). Mercury was determined by adding the $SnCl_2$ reducing solution to the soil digest and measuring the generated mercury vapor with a Perkin-Elmer Model 303 atomic absorption spectrophotometer.

The pyrolysis experiment was conducted in a manner similar to that described by Dudas and Pawluk (1976). A series of triplicate aliquots of ground air-dry organic and mineral soil materials, each weighing from 1.0 to 2.0 g were placed in porcelain crucibles and heated in a muffle furnace at the desired temperature for 4 hours. The initial content of mercury in samples prior to heat treatments was established by analyzing triplicate portions of each of the various soil horizon samples. Temperature treatments ranged from 60 to 300°C. The heated samples were analyzed for total mercury using the flameless method as previously described for other samples.

Samples of washed and unwashed poplar leaves from the Ellerslie study area were analyzed for mercury in order to assess mercury accretion on vegetation from dry deposition.

Leaf samples were washed in three ways. The first method of washing was with a dilute household detergent (1% Ivory) followed by distilled water, the second method was with a dilute laboratory detergent (1% Cationox) followed by distilled water, and the third method was with distilled water only. Washed and unwashed leaves were then analyzed for total mercury after grinding in a Wyllie-mill.

IV. RESULTS AND DISCUSSION

The objective of this study was to evaluate the gains, losses, and seasonal balance and fluctuations of mercury associated with surface soil horizons of forested soils. Inputs of mercury to the surface soil horizons were thought to consist of forest vegetation, rainfall, soil gases, and dry deposition. These were assessed by monitoring levels of mercury in aspen leaves and understory vegetation, in canopy drip and open field precipitation, in washed and unwashed leaves, and in soil gases during the growing season. Potential loss or negative enrichment of mercury was assessed by monitoring levels of mercury in freshly fallen leaves as they decomposed in the laboratory and in the field. The balance of mercury in the surface horizons was monitored to ascertain changes that may occur during the growing season. Information on the form of mercury in the litter layer was evaluated with the pyrolysis experiment.

A. Inputs of Mercury

Mercury in aspen leaves

Aspen leaves were monitored for total mercury during the growing season. Leaf samples were collected periodically from both study areas during the growing season and analyzed for total mercury in order to ascertain the possible translocation of mercury from the rooting zone through the plant and then back to the soil surface through the deposition of leaves in the fall season. Four leaf samples

each a composite from three to five different trees were collected at various dates at each study area during the growing season of 1977.

The total content of mercury in leaves from the Ellerslie study area and from the Cooking Lake moraine study area are shown in Figures 3 and 4, respectively. The average content of mercury in leaves from the Ellerslie study area sampled in early June was 40 ppb Hg, but then dropped to 32 ppb Hg by mid June. From the end of June, average abundances of the element in leaves increased to 59 ppb Hg by the end of July. In early August, the total content of mercury in aspen leaves dropped to an average of 41 ppb Hg. The maximum average content of mercury (78 ppb) occurred in samples collected in September, just as leaves were shed.

The levels of mercury in aspen leaves from the two study areas followed similar patterns during the growing season of 1977 (Figures 3 and 4) which suggested the fluctuations in levels of mercury were not just random variations. At both study areas, the content of mercury in leaves were at minimum levels at the end of June and beginning of July. Levels of mercury increased in late July and then dropped in August. Maximum content of mercury was reached at the time the leaves were shed in September.

The percentage of carbon and nitrogen in aspen leaves at both study areas were monitored during the growing season and are given in Appendix I. The content of carbon and nitrogen in leaves decreased gradually during the summer

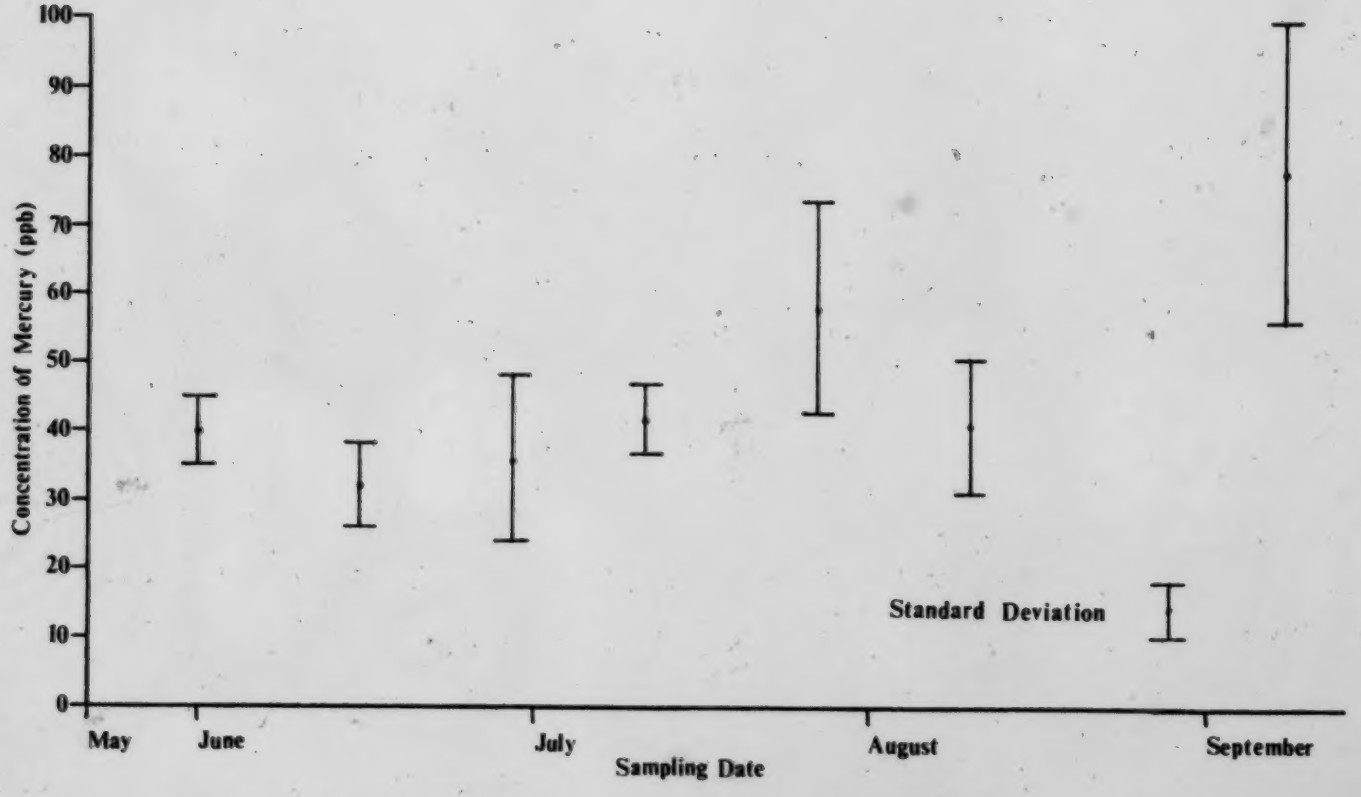

Figure 3. Total content of mercury in aspen leaves from the Ellerslie study area.

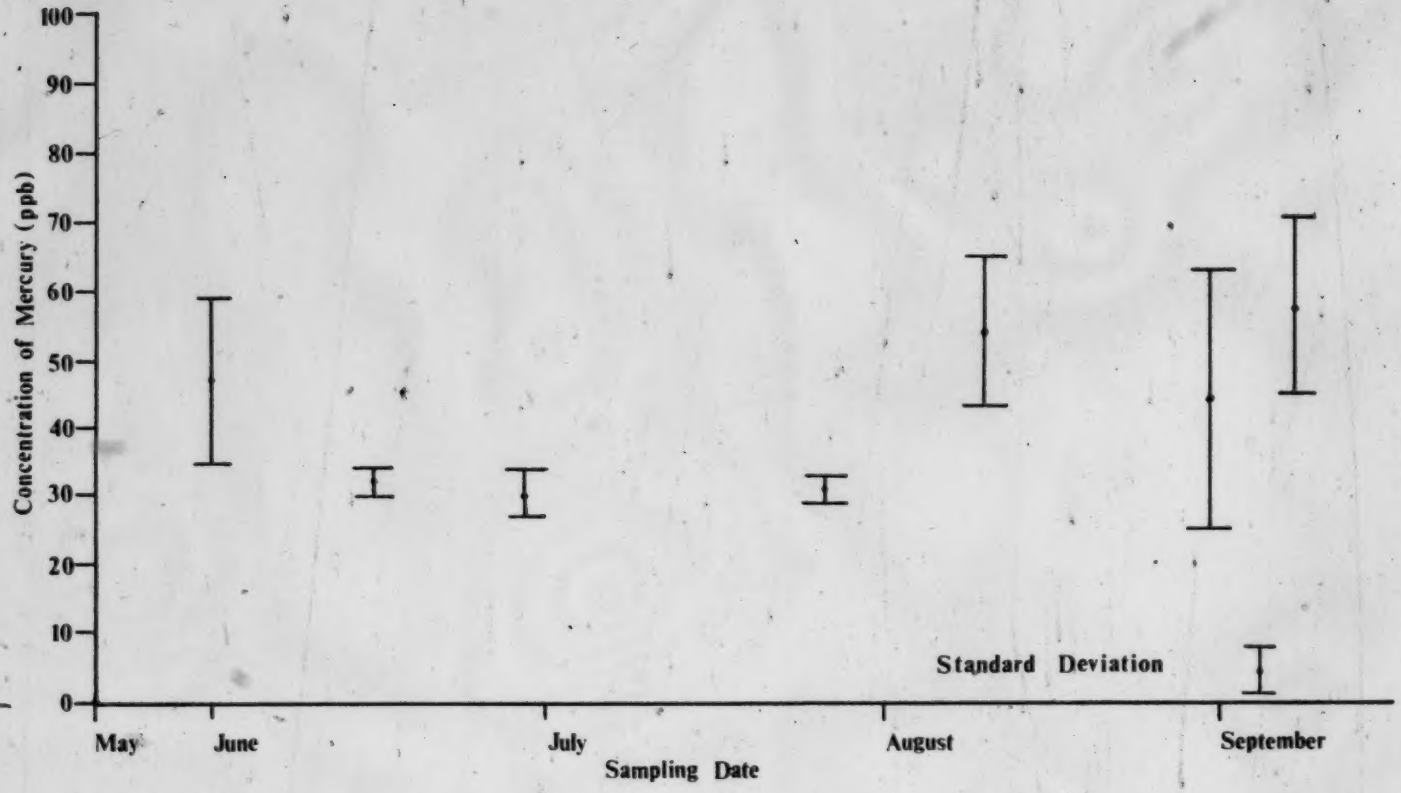

Figure 4. Total content of mercury in aspen leaves from the Cooking Lake moraine study area.

from 51% and 2.8% for carbon and nitrogen, respectively, to minimum values of 41% and 1.4% for carbon and nitrogen, respectively, in mid September for both study areas.

Statistical analysis (coefficient of determination) of the data showed levels of C, N, and Hg and their trends during the growing season were similar for both study areas (Table 3). At each site mercury was significantly correlated with carbon while only with nitrogen at the Ellerslie site (Table 4).

Levels of mercury in samples of aspen leaves collected from Ellerslie and Cooking Lake study areas can not be compared to samples from other areas since there are only a few published studies involving mercury uptake by plants and most samples were collected over mineralized areas. Major work on this subject was done in British Columbia to study the geochemistry of mercury as applied to prospecting (Warren *et al.*, 1966). Levels of mercury in first year leaves of *Populus tremuloides* were measured to be 9 ppm at the old smelter of Pinchi Lake and 4 ppm downwind from the old smelter. Measurements of soil mercury indicated the presence of mercury anomalies. Most measurements of total mercury in plants are determined on samples collected from mineralized areas and therefore little is known about background levels of mercury in unmineralized areas.

A partial explanation for the high levels of mercury in leaves in the later part of the growing season could be negative enrichment with weight loss as certain substances

Table 3. Coefficient of determinations calculated from data obtained from samples of aspen leaves.

Paramaters comparing samples of the two study areas	Coefficient of determination (r^2)
Levels of Mercury	0.67 *
Percentage of Nitrogen	0.66 *
Percentage of Carbon	0.94 *

* significant at the 1% level

Table 4. Coefficient of determinations calculated comparing levels of mercury to percentage of carbon and nitrogen for each study area.

Paramater compared to levels of Mercury	Coefficient of determination (r^2)	
	Ellerslie	Cooking Lake
Percentage of Carbon	0.21*	0.36**
Percentage of Nitrogen	0.49**	0.08***

* significant at the 5% level
** significant at the 1% level
*** not significant at the 10 % level

are translocated back to the tree before leaf fall. Nitrogen, phosporous, and potassium are found in smaller concentrations in freshly fallen leaves compared to green leaves because of translocation of substances containing these elements from the leaves to the wood parenchyma for storage before leaf fall (Kittredge, 1948). However, there is insufficient total N, P, and K in the leaf to account for the nearly two fold increase in the content of mercury in the leaves during the growing season.

Another possibility for the fluctuations and the late season increase in content of mercury of the leaves is that plant available levels of mercury vary during the growing season with more mercury available for plant uptake towards the fall season. The amount of mercury available and taken up by plant roots depends in part on the chemical form of mercury. For example, roots of plants absorb gaseous mercury more easily than they do ionic inorganic mercury (Dolar *et al.*, 1971; Kothny, 1973). Seasonal trends in soil moisture and temperature can affect the levels of gaseous mercury since mercury compounds in the soil could be converted to vaporous forms upon drying and heating. In addition to mechanisms involving root uptake, gaseous mercury in the soil can be released into the atmosphere by diffusing upwards through the soil profile. Vegetation surfaces may then adsorb the released mercury from the atmosphere (Siegel *et al.*, 1974; Lindberg *et al.*, 1979; Huckabee and Janzen, 1975), thereby contributing to the

fluctuating and at times higher than normal background levels of the element detected in the aspen leaves of this study. Documentation and discussion of gaseous soil mercury emanations and its possible contributions to levels in vegetation will be presented in a later section.

Fluctuations in the measured quantity of mercury in the leaf samples may also reflect the daily to seasonal variation of the equilibrium level established between mercury that is translocated to the leaf from the root system and the mercury that is lost from the leaves through evapotranspiration. Mercury is known to be taken up by roots, translocated to the leaves and then returned to the atmosphere in gaseous form (Siegel *et al.*, 1973; Jackson, 1973). Transpiration from vegetation occurs within the first few minutes of sunrise when the stomata open and release mercury that has accumulated throughout the night (Kothny, 1973). Even under conditions of a uniform rate of root uptake and translocation, levels of mercury in the leaf would likely fluctuate due to daily and seasonal variations in transpiration. When warm, dry atmospheric conditions prevail, the plant transpires more and the levels of mercury in the leaf may diminish, whereas when cool, moist conditions prevail the plant does not transpire as much and the content of mercury in the leaf may increase.

The amount of mercury in the leaf and its fluctuations most probably can be explained by a model which involves all the above mentioned processes. Throughout the growing season

mercury is taken up by the tree in variable quantities depending on plant availability and form of the element and is translocated to the leaf through evapotranspiration. In addition to root uptake leaves are also capable of adsorbing variable amounts of gaseous mercury depending on atmopspheric mercury levels. These three processes are believed to account for the observed fluctuations in the amount of mercury in aspen leaves. The extent or importance of each process is fundamently related to seasonal variations in temperature and moisture of both the soil and atmosphere.

Mercury in forest understory

Although poplar seemed to be the main source of organic debris of LFH horizons, understory vegetation was moderately dense at both sites and could serve as a significant input or cycling agent of soil mercury. Accordingly, a number of replicate samples of common understory species were collected from both areas during the spring and early summer and analyzed for mercury.

Results for the analyses (Table 5) can be arranged into three categories consisting of species (dogwood, wildrose, bunchberry) that contain a relatively low content of mercury (20 to 30 ppb Hg), species (wintergreen to wheatgrass) with intermediate levels (30 to 60 ppb Hg), and a third grouping (moss, fungi, mushrooms) with the highest abundance of mercury.

Table 5. Total content of mercury in forest understory vegetation

Sample	number of samples	source*	Mercury content (ppb) range	mean
Dogwood	6	Ell & Ck	17 - 30	22
Wildrose	4	Ell & Ck	20 - 29	25
Bunchberry	4	Ell & Ck	20 - 29	25
Wintergreen	4	Ell & Ck	46 - 62	54
Twinflower	3	Ell & Ck	35 - 50	40
Bedstraw	3	Ell	33 - 50	40
Wheatgrass	4	Ell	27 - 41	34
Moss	5	Ell	77 - 86	80
Bracket fungi	3	Ell	90 - 139	121
Mushrooms	6	Ell & Ck	82 - 159	107

* Ell = Ellerslie study area
Ck = Cooking Lake moraine study area

Reasons for the differences in levels of mercury in the three apparent groupings include ion uptake, rooting habit, and nearness of vegetation to the ground surface. Mercury is taken up during the process of ion uptake by plants, but levels of mercury in the plant tissue are usually lower than in the substrate upon which they grow. Evidence indicates there is a root barrier to translocation of mercury to the plant top. Levels of mercury in plants are higher in the roots than in the tops (John, 1972) and plants appear to largely exclude mercury during the process of ion uptake from the soil (Lisk, 1972). It also appears that movement of mercury within the foliage (such as from the leaf margin to leaf interior) and stems is greater than that from the roots upward (Smart, 1968).

The accumulation route of mercury in mushrooms species, like most other plants is still not known. However, a study by Minagawa (1980) suggests one of the main routes of accumulation could be through adsorption of mercury from the atmosphere. Mushrooms were exposed to mercury vapor and then parts of the mushroom were analyzed for mercury. The plait of the mushroom cap contained the most mercury followed by the flesh of the cap, then the cuticle, and then the flesh of the stalk. It was also found that mercury content increased with exposure to the mercury vapor.

Rooting habit may also influence levels of mercury in the plants. The first two groups of understory vegetation obtain their nourishment by absorbing water and dissolved

nutrients from the soil mineral layer which contains lower levels of mercury as compared to the organic surface horizons above them. The third group of vegetation obtains its nourishment by osmotically absorbing the products of organic breakdown and decay. Higher levels of mercury are found in the organic surface layers as compared to the mineral horizons below them. The organic surface layers serve as a substrate medium for the mosses, fungi, and mushrooms, which act as bioaccumulators of mercury.

The nearness of the vegetation to the ground may also affect the content of mercury in plants and account for the three groupings in Table 5. As mercury is released to the atmosphere, for example by degassing of the soil, the element may be absorbed by the plants. However, since released mercury is dispersed rapidly and diluted with increasing altitude above the soil surface, those plants nearest to the ground surface (the third group shown in Table 5) are more likely to adsorb greater quantities than tall plants (first and second groups of Table 5) which are further away from the source of mercury emanations.

Unlike the first two groups of plants the basidiomycetes, lichens and mosses at the Ellerslie and Cooking Lake study areas accumulated mercury to a greater extent. This third group of vegetation acts as bioaccumulators in that it contains more mercury than its substrate medium. In a study of distribution of mercury between soil and other supportive media and life forms

associated with them, Siegel and Siegel (1973) showed that lower plant life forms were enriched with mercury. Their study indicated that levels of mercury in mosses were enriched about 6 times compared to soil or supportive media, lichens about 8 times, and basidiomycetes about 3.5 times.

The significance of understory vegetation to the return and/or retention of mercury in soil is difficult to determine since understory vegetation was not sampled at leaf fall stage. However, except for magnitude, it is anticipated that the contribution of mercury by the low group (20 to 30 ppb Hg) species at leaf fall to the soil is similar to the contribution of mercury from the aspen leaves. Most of the litterfall in the field occurred from the beginning of September to mid October as observed in a study of total litterfall in 1979 at the Ellerslie Research Station (Sanborn, 1981). *Populus* species accounted for over 82% of the total with *P. balsamifera* being the dominant component comprising about 75% of the total litterfall. Forest understory vegetation comprised less than 18% of the total litterfall, with *Cornus stolonifera* as the dominant shrub and accounting for 16.3% of the total litterfall. The contribution of the intermediate group (30 to 60 ppb Hg) of understory vegetation is also likely to be like aspen leaves at leaf fall. The low and intermediate groups of understory species as well as the aspen leaves constitute a net addition of mercury to the organic surface horizons since the mercury in the vegetation was likely obtained by the

roots from lower depths in mineral soil or by direct adsorption from the atmosphere.

The contribution of the high group (moss, fungi, and mushrooms) of understory vegetation at leaf fall is probably only partially like the contribution of aspen leaves. Instead of representing a net addition of mercury to the soil surface, this group of vegetation may act as retainers of mercury already present in the litter layers. Additionally, since this group of vegetation is also known to adsorb mercury from the atmosphere (Minagawa, 1980; Huckabee and Janzen, 1975) they also contibute to a net addition of mercury to litter layers.

Mercury in rainwater

Raingauges were placed at the Ellerslie study area and canopy drip was analyzed during the spring and summer of 1978. Precipitation outside the forest cover was also collected and monitored for mercury.

Accurate evaluation of the abundance of mercury in rainwater can be adversely affected by certain problems which arise during collection of samples. Solid debris, such as airborne soil material, may be trapped or washed out into collection containers thereby adding to the apparent mercury levels of the liquid sample. Some or even a significant portion of the mercury in collected rain samples may become adsorbed onto the walls of the collection device causing an underestimation of mercury levels. Substantial loss of mercury from collected rainwater may occur in the field

through volatilization of the element via chemical reductive reactions and/or biological methylation particularily when samples remain in the field for extended periods (Jenne and Avotins, 1975; Avotins and Jenne, 1975).

Event sampling was conducted in this study to alleviate or minimize the aforementioned problems. Dry deposition during periods of non-precipitation was thereby avoided and the time during which collected rain remained in the field was kept to a minimum. The consequences of avoiding dry deposition will be pointed out later in the thesis. Additionally, $KMnO_4$ was placed in the raingauges to prevent reduction and subsequent volatilization of mercury. The oxidant also served as a swamping agent for adsorption sites and in all liklihood, provided an undesirable environment to microorganisms.

The rainwater sampling phase consisted of a total of 14 sampling events of 13 discrete rainfalls from early May until the end of August. For each sampling event, five replicates of canopy drip and five replicates of open air precipitation were collected and analyzed for mercury. None of the samples contained detectable quantities of mercury. After the first two sampling events, it was thought the apparent absence of mercury might be due to volatilization loss from containers, possibly caused by ultra violet photodecomposition (Jonasson, 1970). To ascertain whether or not volatilization loss was responsible, all containers were spiked with a small, known amount of mercury (as $HgCl_2$

solution) at the onset of each sampling event. Upon analysis, rain samples consistently contained amounts of mercury equivalent to the quantity added in the spike. The complete recovery of spiked mercury suggested loss, via volatilization or other mechanisms, was not a factor. Instead, levels in rainwater must have been less than the detection limit of the method used in this study.

Although there are data for levels of mercury in air over mineralized and non-mineralized areas there is a paucity of information for levels of mercury in rainwater over these same areas. It is expected, however, that levels of mercury in precipitation would be lower over non-mineralized areas and would increase over mineralized or contaminated areas. The levels of mercury in rainwater of the world range from 0.05 to 0.48 ppb with a mean of 0.20 ppb (Jonasson and Boyle, 1972). Levels of mercury in Canada range from 0.1 to 0.3 ppb (Sherbin, 1979). Geochemical investigation on atmospheric precipitation in Gottinger, F.G.R., a non-industrial medium sized city situated in a rural area, indicated that levels of mercury in rainwater ranged from 0.023 to 0.075 ppb with a mean of 0.039 ppb (Ruppert, 1975). In Sweden the levels of mercury in rainwater were 0.33 ppb (Brune 1969) suggesting contamination of mercury in the environment.

The dection limit of the analytical procedure used in this study to determine levels of mercury in canopy drip and open air precipitate was 0.01 ug Hg. Since 100 mls of

samples was analyzed, there was less than 0.1 ppb Hg present in the rainwater. The maximum amount of mercury that might be returned via rainwater to the Ellerslie study site was calculated to be 410 ug/m^3/year (4.1 g/ha/year) considering that the average rainfall at Ellerslie is about 41 cm and assuming that the concentration of mercury in rainwater is just at the detection limit. This level is higher than the amount of mercury deposited onto the soils of Sweden by rain which was reported to be 1.2 g Hg/ha/year (Andersson and Wiklander, 1965). If 4 g/ha/year of mercury was added to a soil with a bulk desity of 1.2 g/cm^3 and to a depth of 2 cm, the annual increase of mercury to the soil by rainfall would be equivalent to a maximum of 17 ppb.

Levels of mercury in canopy drip under a beech forest in the Solling mountains of Central Germany averaged 0.024 ug/liter (Heindrichs and Mayer, 1977). The average concentration of mercury in the nearby open air precipitation was 0.035 ug/liter. The decrease of mercury in the canopy drip as it passed through the tree canopy suggested that mercury was adsorbed onto the leaves, twigs, and bark of the trees. Mercury was not detected in the nearby open air precipitate at the Ellerslie study area suggesting that no additional mercury was adsorbed by the canopy as the precipitate passed through.

Mercury adsorbed on vegetation

Samples of washed and unwashed aspen leaves from the Ellerslie study area were analyzed for mercury to determine

the extent of accumulation of the element on vegetation by dry deposition. Data for the total content of mercury in washed and unwashed aspen leaves are shown in Table 6. Each value represents the average of triplicate analyses. Samples of leaves were collected June 28 and July 5 during the growing season of 1978. There was no rain for 7 days prior to June 28 and for 6 days prior to July 5. Dust was not visible on the leaves at the time of sample collection.

Samples of unwashed leaves collected in June contained 36 ppb Hg (Table 6). Levels of mercury in washed leaves were essentially the same as in unwashed leaves. Statistical analysis showed there was no significant difference in the content of total mercury between washed and unwashed leaves for either of the two sampling dates.

Results of this phase of the study indicated dry deposition of mercury on vegetation surfaces prior to the two samplings did not occur and its importance as an input of mercury into the forest litter remains unclear. Only two samplings were involved in the evaluation of dry deposition; however, results for canopy drip collected throughout the growing season also suggests accretion of mercury containing particulates on leaves is unlikely or at a rate below that which can be detected by the methods of this study.

Johnson and Braman (1974) reported on atmospheric speciation of mercury in Tampa Bay, Florida. Their study and others indicate that about 90% of the mercury in air is "volatile" and less than 10% is in "particulate" form. This

Table 6. Total content of mercury in washed and unwashed aspen (*Populus tremuloides*) leaves.

		Mercury content (ppb)			
		June 28		July 5	
Treatment*	Number of replicates	range	mean	range	mean
1	3	33 - 38	36	35 - 40	37
2	3	34 - 39	36	35 - 40	37
3	3	32 - 40	37	31 - 41	36
4	3	30 - 38	35	31 - 40	35

* 1 = none

2 = distilled water

3 = household detergent and distilled water

4 = labotatory detergent and distilled water

low level of "particulate" mercury in the air suggests that dry deposition of mercury onto vegetation and soil may not be as significant as the process of direct adsorption of mercury from the atmosphere. The latter return process is exceedingly difficult to evaluate and attempts were not made in this study to single out the contribution via direct adsorption.

Return of mercury in the atmosphere to the landmass could also occur through washout of mercury vapor by snow or by dry deposition of mercury onto snow surfaces. Normal background levels of mercury for the world in snow are reported to be in the range of less than 0.005 to 0.05 ppb with a mean of 0.01 ppb (Jonasson and Boyle, 1972). These levels of mercury in snow samples are below the detection limit of the method used to determine concentrations of mercury. Therefore, the amount of mercury in snow was not determined in this study.

Return of mercury to the earth's surface through either dry deposition or precipitation was not detected in this study and a portion of the global cycle of mercury (Figures 1 and 2) seems unexplained. However, mercury in the atmosphere most probably returns to the land surface by all the known mechanisms (dry deposition, rainfall, snowfall, and direct vapor adsorption), but the amounts and rates occur at or below detection limits at the two study areas.

Mercury in soil gases

A part of the global cycle of mercury (Figures 1 and 2) involves a subcycle where mercury in the atmosphere is returned to the soil through rain, dry deposition, or direct adsorption. Mercury in soil can then be released back to the atmosphere through degassing of the soil. Measurements of the flux of mercury from the soil to the atmosphere are relatively new and not well documented. However, these measurements are exceedingly important in the understanding of the complete global cycle of mercury.

The flux of gaseous mercury measured above each of the L, F, H, and Ah horizons during 1978 and 1979 at the Ellerslie study area are shown in Table 7, while the flux of gaseous mercury above each of the L, F, H, and Ae horizons during 1979 at the Cooking Lake moraine study area are shown in Table 8. Each value represents the average of triplicate field measurements.

Similar patterns for the flux of gaseous mercury measured above the litter and mineral soil horizons occurred for each study area. Emanations of gaseous mercury measured directly above the L, F, and H litter horizons and Ae and Ah mineral horizons were low or not detected during most of the spring and summer, but increased dramatically during August and September to a maximum of 4.9 ug/m^2/day. The flux of mercury rapidly diminished during October and was no longer detected in November. The late summer and fall release of gaseous mercury in the study seems related to seasonal

Table 7. Flux of mercury in soil gases collected above the surface soil horizons at Ellerslie study area (1978 and 1979)

Monitoring date	Collection interval (days)	Hg flux (ug/m²/day) L	F	H	Ah
1978					
July 25	8	N.D.*	N.D.	N.D.	N.D.
August 4	7	N.D.	N.D.	N.D.	N.D.
August 18	10	2.2	2.2	2.5	2.5
August 28	10	2.2	0.8	1.7	1.7
October 7	8	4.2	4.3	4.4	4.4
October 18	7	1.6	2.0	1.6	0.8
November 2	7	N.D.	N.D.	N.D.	N.D.
1979					
May 29	8	N.D.	N.D.	N.D.	N.D.
June 20	9	N.D.	N.D.	N.D.	N.D.
July 17	8	N.D.	N.D.	N.D.	N.D.
August 9	10	N.D.	N.D.	N.D.	1.4
August 17	8	3.1	4.9	3.1	1.4
September 16	9	2.8	3.2	3.0	2.8
October 29	10	N.D.	N.D.	N.D.	N.D.

* Not Detected

Table 8. Flux of mercury in soil gases collected above the surface soil horizon at Cooking Lake moraine study area (1979).

Monitoring date	Collection interval (days)	Hg flux (ug/m²/day) L	F	H	Ae
May 29	8	N.D.*	N.D.	N.D.	N.D.
June 2	4	N.D.	N.D.	N.D.	N.D.
June 12	8	N.D.	N.D.	N.D.	N.D.
June 20	8	N.D.	N.D.	N.D.	N.D.
July 10	8	N.D.	N.D.	N.D.	N.D.
July 17	7	N.D.	N.D.	N.D.	N.D.
August 9	10	N.D.	4.9	4.9	N.D.
August 17	8	3.2	4.8	4.7	1.0
September 16	9	2.8	3.5	3.5	3.5
October 29	10	N.D.	N.D.	N.D.	N.D.

* Not Detected

trends in soil moisture and temperature. The purge of gaseous mercury occurs at a time when the soil is driest and warmest. For example, in 1979, soil temperatures at 100 cm depth at the Ellerslie study area peaked in July with an average monthly temperature of 8°C, while temperatures at the 20 cm depth also peaked in July at an average montly value of 12°C. Soil temperatures at the 3 meter depth reached a maximum of 8.8°C in October (data from the Ellerslie Meteorological Station records).

In 1978, soil temperatures at the 100 cm depth reached a maximum in August averaging 11.5°C, peaked at the 20 cm depth in July at 14.4°C and peaked at the 3 meter depth in August at an average montly value of 9.5°C (data from the Ellerslie Meteorological Station records).

In 1979, soil moisture at the Ellerslie study area continually decreased reaching a minimum in the month of August, when the soil was too dry to measure in the B horizon (Sanborn,1981). In 1978, soil moisture in the B horizon became too dry to measure during the month of July.

These moisture and temperature patterns could well explain the purge of gaseous mercury observed during the fall season. A study by Jones and Hinesly (1972) suggests that as the soil becomes more areated at depth mercury compounds that were stable under anaerobic conditions are converted to volatile vaporous forms which diffuse through the profile to the atmosphere.

There are two possible sources to explain the origin of the mercury collected on the copper foil. The first is that mercury is degassed at depths below the soil profile and then diffuses upward to the atmosphere. The second is that mercury is released to the atmosphere from the organic soil horizons as microbial decomposition occurs. Using 1978 data for the Ellerslie study area the total flux of gaseous mercury was determined to be 90 ug Hg/m^2 over the time period from August 8 to October 18. If the litter horizons had a bulk density of 0.5 g/cm^3 and the depth of the litter horizons was 20 cm there would be 100,000 grams of LFH material in one square meter. Using 90 ug Hg/m^2 as the flux and 100,000 grams as the weight of soil, the amount of mercury that would have to be degassed from the soil would be 0.9 ppb Hg. This calculation illustrates that the purge of mercury during the fall season represents only a small amount of the element. If this mercury originated from the decomposition of the organic soil horizons the flux should have been noticed earlier in the season when microbial activity would have been greater. The most probable source of mercury is degassing which occurs continually at depths below the soil profile. Its upward migration and release to the atmosphere appears to be influenced by seasonal variations of soil moisture and temperature.

B. Losses of Mercury

Laboratory decomposition study

Freshly fallen leaves were brought into the laboratory and allowed to decompose to determine if negative enrichment accompanied the microbial decomposition of the leaf material. Measurements of total content of mercury, organic carbon, and nitrogen in decomposing leaf material were started in May 1978 and completed at the end of April 1979. Data for the total content of mercury in decomposing leaf material collected from the Cooking Lake moraine study area and the Ellerslie study area are shown in Figures 5 and 6.

The general trend for the levels of mercury in decomposing leaves are similar for leaf samples from the two study areas. There was a slight decrease in content of mercury through the first three months of the study followed by a progressive increase in levels of mercury throughout the duration of the experiment. Initially, the leaves collected from the Cooking Lake study area contained 79 ppb Hg. After decomposition for three months, the levels of mercury in the leaves decreased to 66 ppb, afterwhich content of mercury increased progressively to values of 250 ppb at the end of the study. Similar values for levels of mercury in aspen leaves collected from the Ellerslie study area occurred during decomposition.

Contents of carbon and nitrogen were also monitored in the aspen leaves to give an indication of the degree of decomposition. The complete data obtained for organic carbon

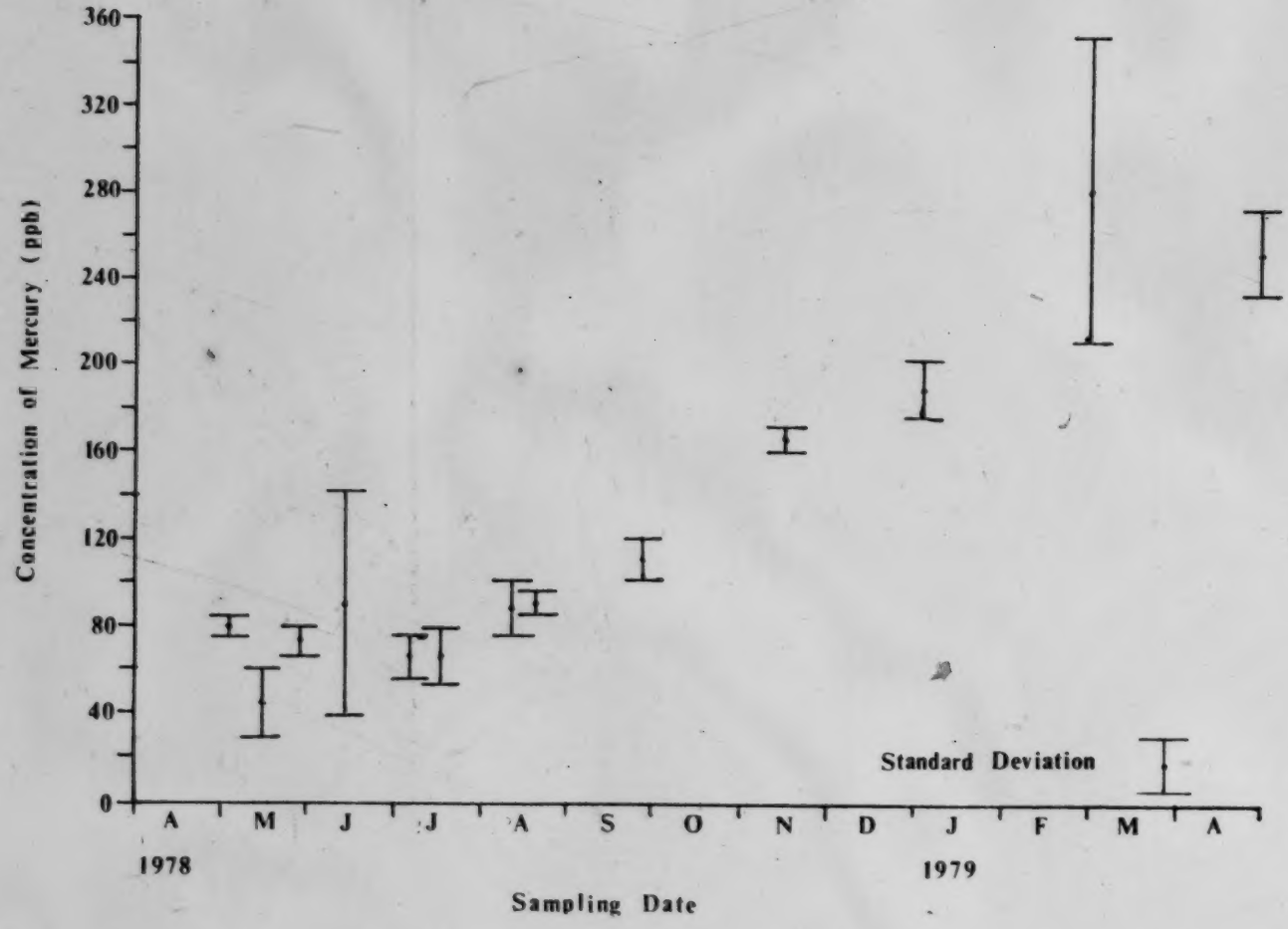

Figure 5. Content of mercury in decomposing leaves from Cooking Lake study area.

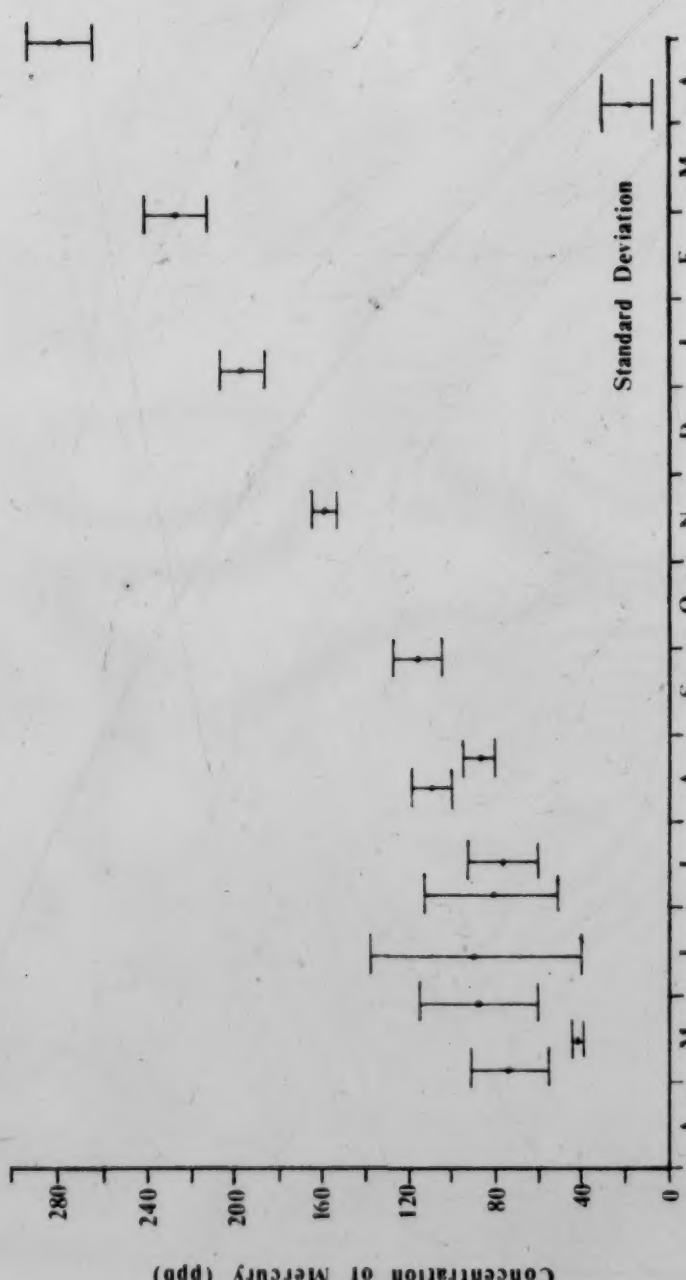

Figure 6. Content of mercury in decomposing leaves from Ellerslie study area.

and total nitrogen is shown in Appendix II. The trends in values of carbon and nitrogen with decomposition were similar for samples of the two study areas. In general, the percentage of carbon in the decomposing leaf samples gradually decreased from 42% at the beginning of the study to 31% at the end. Percentage of nitrogen, however, increased from about 1.0% to about 2.0% throughout the duration of the study. The C/N ratio decreased progressively throughout the microbial decomposition of the aspen leaves from 48 to 15. Mercury was not significantly correlated with carbon for the Cooking Lake samples but was for the Ellerslie samples. Mercury was significantly correlated to percentage of nitrogen and C/N ratio (Table 9).

Data for mercury in decomposing leaf material, with 10 mg added N, for both Ellerslie and Cooking Lake samples are shown in Figures 7 and 8. The general trend in mercury levels with decomposition is similar to the trend without added nitrogen. Contents of carbon and nitrogen were monitored; the data appears in Appendix II. The general trends for contents of carbon, nitrogen, and C/N ratio during decomposition for the nitrogen spiked samples are similar to those trends seen for samples without added nitrogen. Levels of mercury in the decomposing spiked leaves from each study area were significantly correlated with carbon, nitrogen and C/N ratio (Table 10).

Levels of mercury in decomposing aspen leaves in the laboratory were significantly correlated to contents of

Table 9. Coefficient of determinations comparing levels of mercury to percentage of carbon and nitrogen and to C/N ratio in decomposing leaves of samples from both study areas.

Paramater compared to levels of mercury	Coefficient of determination (r^2) Ellerslie	Cooking Lake
Percentage of carbon	0.18*	0.04**
Percentage of nitrogen	0.81***	0.69***
C/N ratio	0.46***	0.56***

* significant at 5% level

** not significant at 10% level

*** significant at 1% level

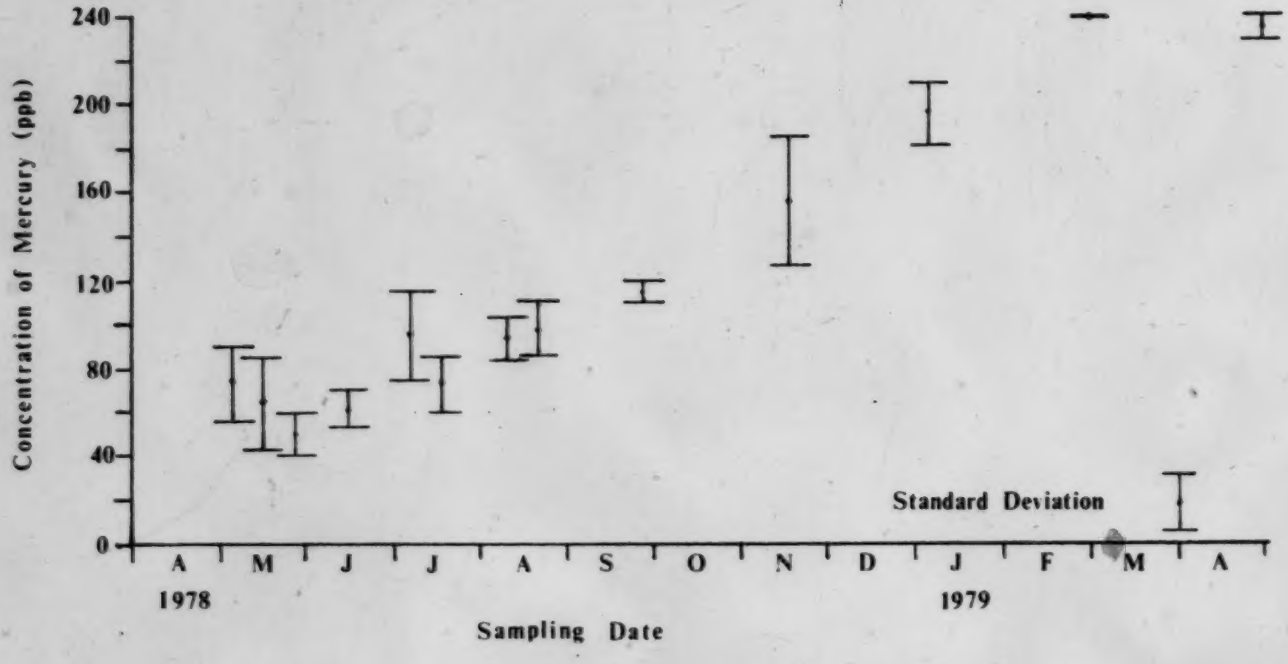

Figure 7. Content of mercury in decomposing leaves, from the Ellerslie study area, with added nitrogen (10 mg).

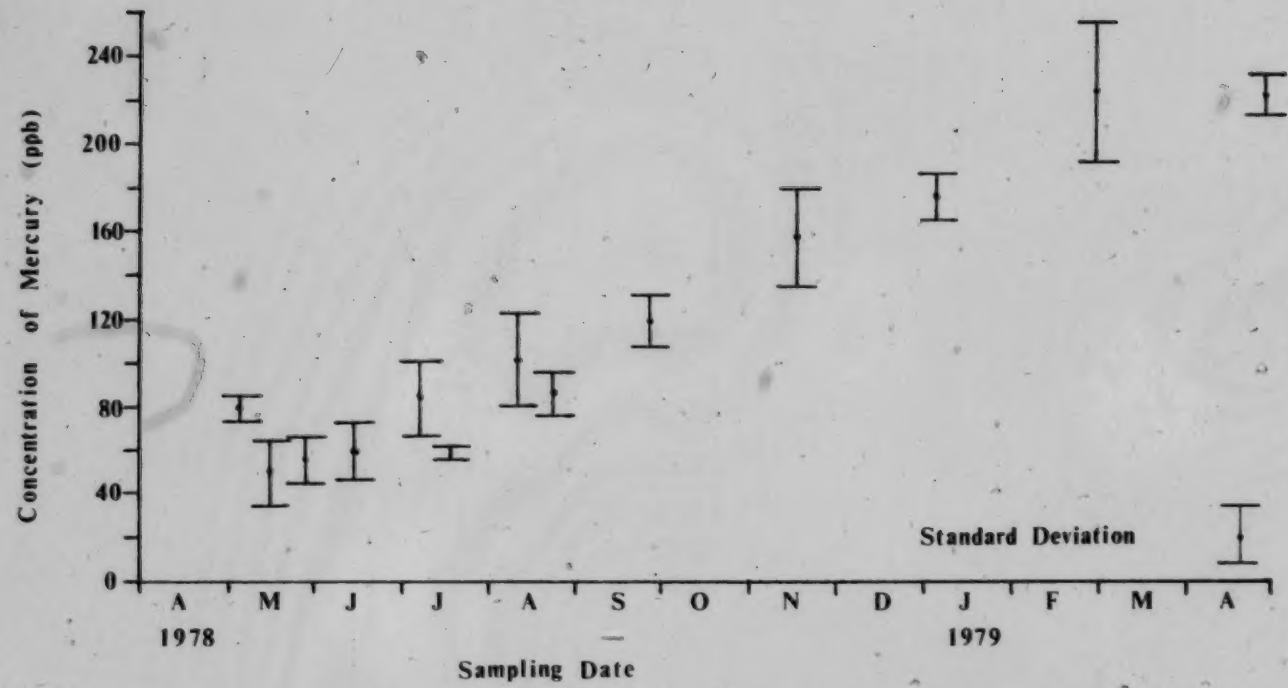

Figure 8. Content of mercury in decomposing leaves, from the Cooking Lake moraine study area, with added nitrogen (10 mg).

Table 10. Coefficient of determinations comparing levels of mercury to percentage of carbon and nitrogen and to C/N ratio in decomposing leaf samples (with added nitrogen) from both study areas.

Parameter compared to levels of mercury	Coefficient of determination (r^2)	
	Ellerslie	Cooking Lake
Percentage of carbon	0.17*	0.29*
Percentage of nitrogen	0.58**	0.76**
C/N ratio	0.49**	0.46**

* significant at 5% level
** significant at 1% level

nitrogen. This correlation probably occurs because the soluble carbon fraction low in content of mercury disappears first as decomposition proceeds, leaving behind an accumulation of nitrogen and mercury due to weight loss of the original sample.

There was no difference in levels of mercury in decomposing aspen leaves in the laboratory between samples that had an added 10 mg N and those that did not. The amount of nitrogen added was not sufficient to promote a sustained burst of microbial activity. Decomposition rates and levels of mercury between the leaf samples with the N spike and those without N addition were similar.

Field decomposition study

Poplar leaves were placed in the field directly above the Ah horizon at the Ellerslie study area and above the Ae horizon at the Cooking Lake moraine study area and allowed to decompose under field conditions. Three separate sites were chosen at each study area for the field decomposition study. Measurements of mercury, organic carbon, and nitrogen were conducted as in the laboratory decomposition study. The leaves in the field at each study area appeared to degrade twice as fast as in the laboratory. The presence of mold and fungi was noticed on the leaves in the field as they decomposed. As the leaves decomposed and broke apart, leaf fragments were mixed into the top portion of the Ah and Ae horizons.

Data for the total content of mercury in the decomposing leaves for the Ellerslie and Cooking Lake moraine study areas are shown in Figures 9 and 10. Generally, although there were some fluctuations, the content of mercury remained close to 60 ppb throughout the decomposition period for both study areas. Average content of mercury for quadruplicate samples varied from 50 to 79 ppb Hg for the Ellerslie study area and varied from 47 to 79 ppb Hg for the Cooking Lake moraine study area. The level of mercury in leaves decomposing under field conditions did not steadily increase as was the case with the laboratory study.

Data for mercury, organic carbon, and nitrogen of the decomposing leaves in the field during the growing season for both study areas is shown in Appendix II. There was a gradual decrease in percentage of carbon in the leaves at the Ellerslie study area with a similar trend for content of carbon in leaves at the Cooking Lake study area. The percentage of nitrogen gradually increased with decomposition for leaves at both locations. Statistical analysis showed that levels of mercury were significantly correlated with content of nitrogen or carbon.

Reasons for the differences in the levels of mercury between decomposing aspen leaf samples in the field and in the lab are not readily apparent. Factors such as differences in the intensity of ultraviolet light, physical mixing of horizons, volatilization of mercury, and leaching of mercury may account for the dissimilarities.

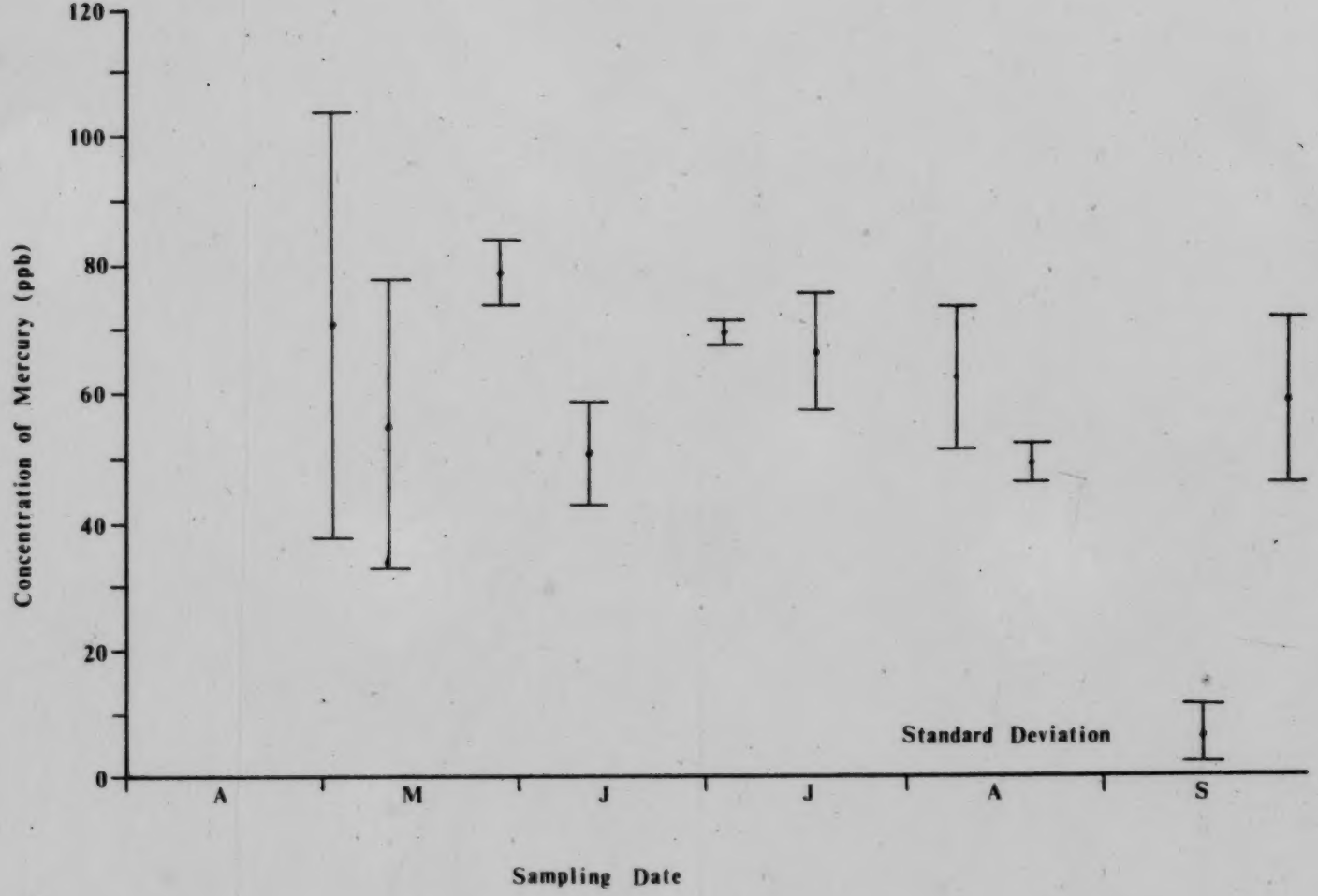

Figure 9. Content of mercury in decomposing leaves in the field at Ellerslie.

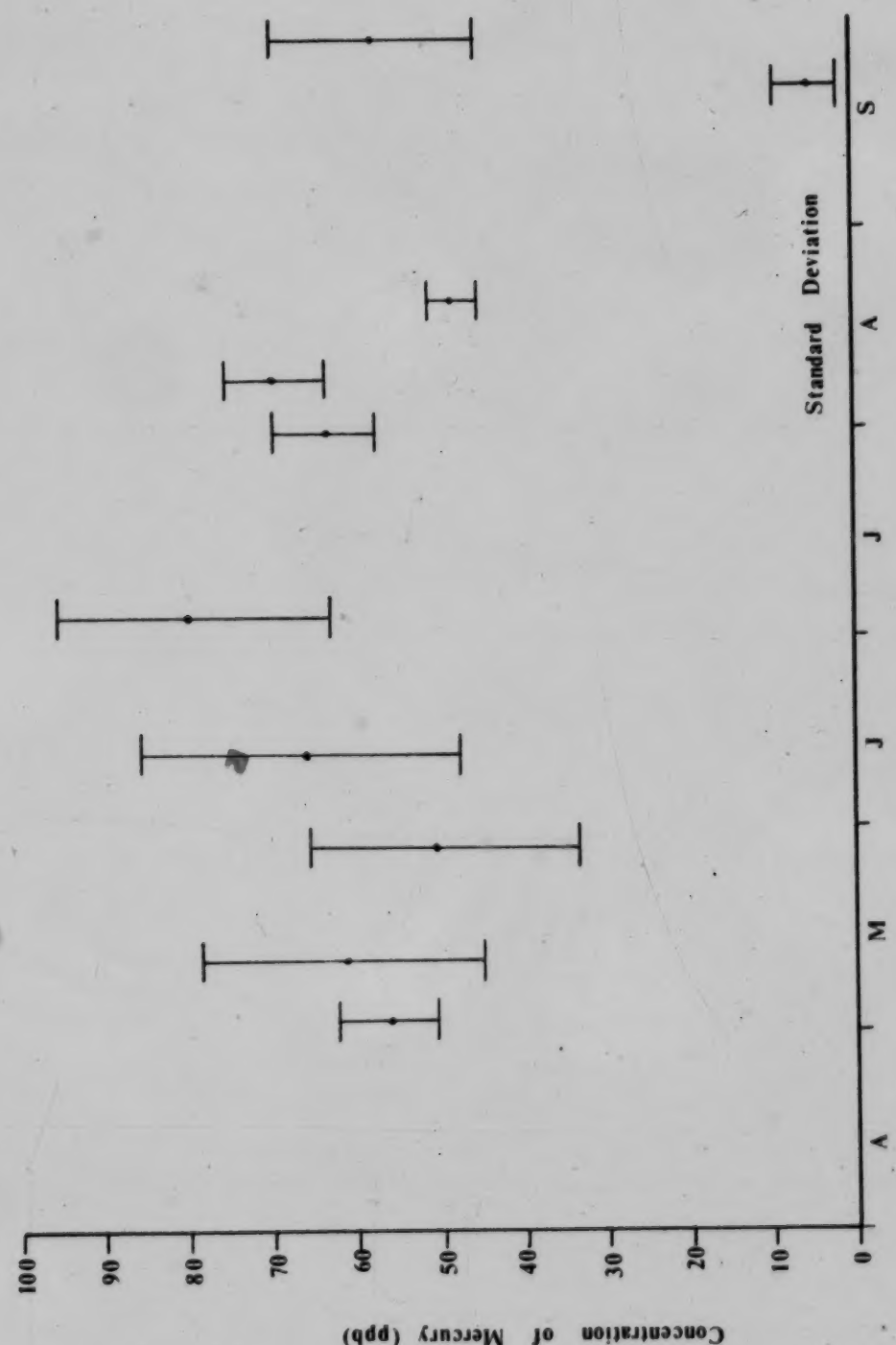

Figure 10. Content of mercury in decomposing leaves in the field at Cooking Lake.

Decomposition of organic mercurials can be carried out by means of ultraviolet radiation. This photodecomposition reaction has been documented in studies where determinations of mercury were made with and without ultraviolet irradiation of mercury containing samples (Kiemeneij and Kloosterboer; 1976). Decomposition of organomercurials by such irradiation results in production of Hg^{+2} which can then be methylated to volatile forms of monomethyl and dimethylmercury. The mercuric ion can also be converted to elemental mercury (Jernelov; 1972). In this study a greater intensity of ultraviolet light in the field compared to laboratory conditions could have caused greater losses of mercury in field samples.

Other possible differences between samples from the field and from the laboratory include physical mixing of horizons and volatilization of mercury from the soil. Physical mixing of leaf material into the underlying Ah horizon occurred in the field. The physical mixing of leaf material into the underlying Ah horizon resulted in lower concentrations of mercury since the Ah mineral horizon contained less mercury than the aspen leaf material. Volatilization of mercury in field samples may have occurred to a greater extent than in the laboratory. Mercury can be released from the soil into the atmosphere through several reactions such as the reduction of the mercuric ion to volatile metallic mercury (Jernelov; 1972) or oxidation of mercury to its bivalent form (Hg^{+2}) can take place, where it

is then converted biologically to volatile monomethyl and dimethylmercury (Jernelov; 1972). Volatilized mercury in the field may have dispersed rapidly into the atmosphere because of air movements. However, in the laboratory, volatilized mercury may have redeposited or readsorbed onto the decaying plant tissue because of the lack of air movement (pans were covered with polyethylene sheets).

Leaching of mercury was initially considered a possible process contributing to the observed differences in contents of mercury in the field and in the laboratory. However, analysis of liquid at the bottom of the decomposition pans did not reveal the presence of mercury. More importantly, levels of mercury in the soil profiles of the two study areas indicates leaching of the element has not occurred (Table 10). Levels of mercury in the lower soil horizons are generally less than the amount originally present in the leaves at the start of the decomposition study. Tripp and Harriss (1978) suggests that as decomposition occurs the soluble cellular fractions which are low in mercury are released first indicating that the mercury is retained in a fraction of the organic tissue which is more resistant to decomposition. Their results also suggest mercury would not be easily or rapidly leached from decomposing plant debris.

At the onset of this study it was believed that high levels of mercury reported in forest litter were due to negative enrichment of the element as the leaf litter decomposed. The concentration of mercury in aspen leaves in

Table 11. Levels of mercury in soil profiles for both the Ellerslie and Cooking Lake study areas.*

Ellerslie		Cooking Lake	
Horizon	Hg (ppb)	Horizon	Hg (ppb)
L	114	L	72
F	85	F	125
H	69	H	60
Aheg	11	Ae	9
Aejg	16	AB	19
Btg	60	Bt1	36
Ckg	58	Bt2	48
		Ck	37

* Samples collected September 18, 1979

the field at the start of decomposition was 71 ppb for Ellerslie samples and 56 ppb for Cooking Lake samples. Initially, in the laboratory decomposition experiment the content of mercury was 73 ppb for Ellerslie samples and 79 ppb for Cooking Lake samples. At the end of equivalent decomposition (using C/N ratios) the comparable concentration of mercury was 160 ppb for Ellerslie lab samples and 60 ppb for Ellerslie field samples in mid November and 110 ppb for Cooking Lake lab samples and 57 ppb for Cooking Lake field samples in late September. Results from the field decomposition study indicate that negative enrichment does not occur in decomposing leaf samples taken from the field. Negative enrichment due to weight loss in decomposing leaves occurs if there are no simultaneous losses of mercury as decomposition proceeds. Assuming no such losses and using the aforementioned laboratory values for levels of mercury to set conservative minimum values due to negative enrichment suggests there is a substantial net loss of mercury in the field samples during decomposition. This net loss is due to the volatilization losses that occur in the field.

C. Seasonal Variations in the Balance of Mercury

Content of mercury in surface horizons at the Ellerslie and Cooking Lake study areas were monitored during 1977 and 1978 to ascertain the nature and extent of possible fluctuations. Total content of soil mercury varied

considerably among the surface horizons of each study area; however, the pattern of variation amongst horizons was similar between samples from the two locations for both years.

The abundance of mercury in surface soil horizons at the Ellerslie study area for 1977 is shown in Figure 11. This data typifies the seasonal behavior of mercury monitored at both study areas for the two years. Each data point in the figure represents the average of analyses of quadruplicate samples. Levels of mercury in the surface organic horizons were relatively high in early spring, then diminished through early June, fluctuated during late June and through July, and reached minimum levels usually in August. Starting at about mid August, levels of mercury in the organic surface soil horizons increased sharply to maximum or near maximum levels in September afterwhich levels declined close to summer levels.

Contents of mercury in L, F, H, and Ah horizons for the first sampling event in early spring 1977 at the Ellerslie study area were 73, 120, 62, and 27 ppb Hg, respectively, and then decreased to minimum values of 54 ppb Hg in late July for the L horizon, 59 ppb Hg in mid August for the F horizon, 37 ppb Hg for the H horizon in mid August, and 15 ppb for the Ah horizon in late June. The levels of mercury in aspen leaves at leaf fall are similar to levels of mercury in the L horizon for the first sampling in early spring . Maximum levels of mercury in L and F horizons

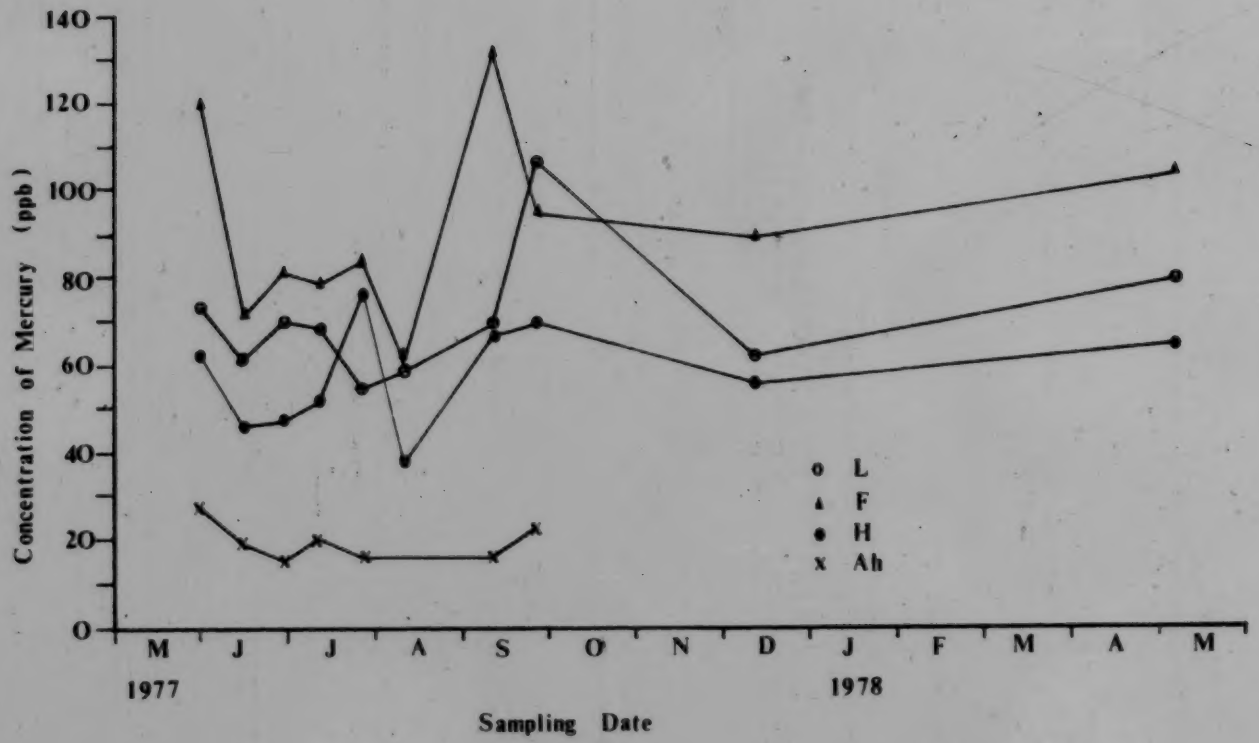

Figure 11. Content of mercury in surface soil horizons at Ellerslie study area.

occurred in September and were 106 and 131 ppb Hg, respectively. Maximum levels of mercury in the H horizon occurred in late July at a value of 76 ppb Hg, while maximum levels of mercury in the Ah horizon were obtained in the first sampling in early June at a value of 27 ppb Hg.

Trends for the content of mercury in surface soil horizons at the Cooking Lake study area (Figure 12) were similar to those at Ellerslie. The only major difference occurs in the F horizon between samples of the two study areas. Levels of mercury in the F horizon from the Ellerslie study area are relatively high in early June and then rapidly decline in mid June and fluctuate in late June and July and reach minimum values in mid August. However, levels of mercury in the F horizon from the Cooking Lake study area are relatively high in early June and remain high until July when values then start to decline reaching minimum values in mid August. Maximum levels of mercury in the H horizon from the Cooking Lake study area occurred in September, whereas in samples of H horizons from Ellerslie maximum levels of mercury were in July.

Content of mercury was higher in the L and F horizon samples collected at the Cooking Lake moraine study area than in comparable samples collected at the Ellerslie study area. This observation may be due to differences in climate and vegetation of the two study areas. Cooking Lake has a cooler, moister climate and is predominantly in a forested area, while Ellerslie is in a grassland area. There would be

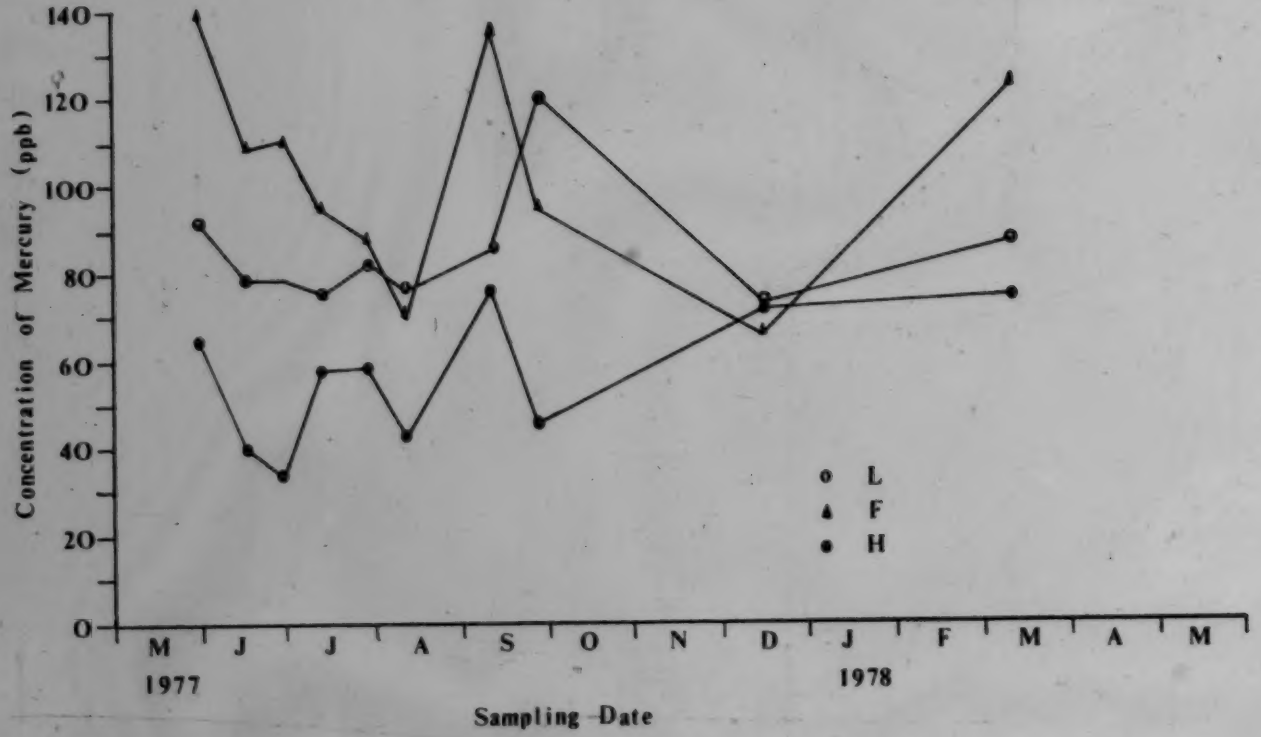

Figure 12. Content of mercury in surface soil horizons at Cooking Lake moraine study area.

less biological activity at the Cooking Lake atudy area resulting in higher levels of mercury in the L and F horizons as compared to Ellerslie. There was no significant difference in content of mercury between samples of H horizons collected from both study areas. The aforementioned difference was also observed again in 1978 samples (Appendix I).

The level of mercury was generally highest in the F horizon and lowest in the Ah horizon at any given sampling date. In general, the L horizon contained higher levels of mercury than the H horizon. Statistical analysis showed that the levels of mercury in each of the L, F, H, and Ah horizons at the Ellerslie study area for the entire season were significantly different at the 1% level. Levels of mercury in each of the L, F, and H horizons at the Cooking Lake moraine study area were also significantly different at the 1% level.

These differences in the amount of mercury amongst horizons are likely due to mercury concentrating in materials resistant to decomposition and volatilization of mercury due to microbial degradation of the more highly resistant materials. In a study by Tripp and Harriss (1978) 90% of total mercury in mangrove leaves was found to be concentrated in cell wall materials which are highly resistant to decomposition and 10% of total mercury was associated with cellular fluids and components which are easily degraded. This investigation suggests that enrichment

of mercury in the F horizon at Ellerslie and Cooking Lake study areas results as the aspen leaves in the L horizon decompose. During early stages of decay of the leaves, soluble cellular fractions which are low in mercury are utilized by microorganisms. This results in an increase in concentration of mercury in the F horizon as the more resistant materials accumulate and form a major part of the organic residues in the forest litter. As decay of the plant material proceeds microbial degradation of the more highly resistant materials such as lignin occurs by basidiomycetes, ascomycetes, actinomycetes, and several groups of bacteria (McLaren and Peterson, 1967). Release of mercury from the soil due to biological activity results in lower levels of mercury found in the H and Ah horizons.

There appear to be seasonal systematic and nonsystematic trends in levels of mercury in litter and Ah samples from the two study areas (Figures 11 and 12). The systematic trend includes relatively high levels of mercury in surface soil horizons in early spring, minimum levels of mercury in late July to mid August, maximum or increased levels of mercury in late summer and early fall, and then a decline in content of mercury in late fall to summer values. These systematic trends reflects the net balance of losses and additions of mercury which in part are controlled by seasonal changes in environmental conditions such as temperature and moisture. Nonsystematic trends or apparently random fluctuations in levels of mercury occur through the

summer months.

In general, in early spring, levels of mercury in the LFH horizon samples are relatively high and then decrease to lower levels of mercury in summer. These relatively high early spring values may be due to low level continual degassing of the earth's crust through the winter. Mercury vapor may slowly permeate the frozen subsoil over the winter months and accumulate in the surface soil horizons. The relatively high levels of mercury in surface soil horizons may also originate from addition of mercury from melted snow. Dry deposition of mercury or direct adsorption of mercury from the atmosphere to snow may occur (Matheson, 1977). As the snow melts mercury is released and temporarily enriches surface horizons.

Levels of mercury diminished during June and then fluctuated in an apparent random manner during the summer months prior to the fall season climb. This June, July, and early August portion of the seasonal pattern likely reflects the combined effects of microbial activity on the volatilization loss of mercury and a constant or intermittent low level source of addition of the element to organic soil horizons. Specifically, the decline in levels during June can be attributed to rapid volatilization loss, probably involving a methylation reaction, in response to the flush of microbial activity which likely ensues as soil temperatures increase from the cold, late winter and early spring conditions. Heating and drying of the soil would by

itself promote desorption of the element and some of its volatile compounds. During the summer months, volatilization of mercury by microbes would continue at rates that would fluctuate partly according to the response of the organisms and their numbers to fluctuating soil climatic conditions. Distribution and form of mercury within the decomposing litter and purely chemical volatilization reactions not directly involving microbes could also contribute to the observed pattern. Since levels of mercury do not continually decline or plateau at some low level during the summer months, one can only conclude that while loss of the element is a constant process, it is also being added to organic soil horizons during the summer months. As mentioned previously, the exact nature and magnitude of all sources of addition were not identified in this study. Low-level sporadic sources, such as multiple gaseous emanations, along with transfers of mercury amongst horizons could contribute to the seemingly random pattern observed in the summer.

Maximum levels of mercury generally occurred in samples of L, F, and H horizons during late summer and early fall as compared to levels encountered during the rest of the growing season. These fall season peak levels of mercury likely arise from the adsorption of gaseous mercury. It will be recalled that a purge of mercury was detected in soil vapor during the months of August, September, and October, with peak values recorded during September. The upward diffusing vaporous mercury is adsorbed on organic matter

accounting for the elevated levels of mercury in the soil during September. These elevated levels of mercury decrease as adsorbed mercury is mobilized to the atmosphere through volatilization processes.

Results of this phase of the study show that changes occur in the mercury status of Luvisolic soils in each of the L, F, H, and Ah horizons during a given year. Most previous studies on soil mercury have dealt with static measurements of total quantity of mercury present in soils to assess normal background levels (Dudas and Pawluk, 1976; McKeague and Kloosterman, 1974). However, this study illustrates static measurements can be quite misleading as there are fluctuations in normal background levels of mercury in a given soil during the seasons. These fluctuations, although not previously documented by others, are not surprising since mercury is well known for its ease of mobility especially in biologically enriched environments.

D. Form of Mercury in Soil

Upon completion of the work dealing with the dynamics of mercury in the two forested sites, it was felt that some characterization data of the form(s) of mercury in the studied samples would be useful as further verification of the diverse nature of soil mercury. The task of elucidating forms of mercury is rendered exceedingly difficult by the potential occurrence of many discrete compounds and

nondiscrete organically complexed forms of the element within a soil. Most methods now available, largely developed for air and water analysis, are suitable for quantifying only single discrete forms such as elemental, methylated and inorganic forms of the element (Trujillo and Campbell, 1975; Baughman *et al.*, 1973; Cappon and Smith, 1977, Elly, 1973).

For practical reasons, "form" of mercury in this study was evaluated using a pyrolysis method originally developed by Koksoy *et al.* (1967) for characterization of geological materials. Their method involves measurement of temperatures at which thermally induced volatilization of mercury occurs from solid samples. Results are plotted as a curve depicting the relative loss of mercury with increasing sample pretreatment temperature. For samples containing a discrete mercury compound, extensive liberation of mercury occurs within a narrow temperature range corresponding to the decomposition temperature of the mercury compound.For samples containing a number of discrete mercury compounds a similar number of inflection points would be observed in the mercury loss plot corresponding to each compound's decomposition temperature.

In this study, samples used for the pyrolysis experiment were composite samples from each of the L, F, H, and Ah horizons prepared by combining samples from both study areas, except for the Ah horizon composite which was prepared from a mixture of Ah samples from the Ellerslie study area only. Composite samples were prepared of each of

the horizons collected in September when contents of mercury in the samples were at an elevated level. Composite samples were also prepared of each of the L, F, H, and Ah horizons collected in July when contents of mercury in the samples were not at an elevated level.

Data for the liberation of mercury from the July samples are shown in Figure 13. Each value representing loss of mercury with heating is the average of triplicate analyses. Loss of mercury from the July samples was first detected at pretreatment temperatures of 60°C. By heating samples to 150°C only about 15% of the total mercury was lost; however, by pretreatment temperatures of 175°C about 50% of the total mercury was liberated. Between 80 to 85% of the total mercury was liberated from July samples when heated to 210°C. At pretreatment temperatures of 300°C mercury was completely liberated from L and F horizons and about 15% of the total mercury remained in the H and Ah samples. Mercury loss patterns for each of the horizons were similar, but samples of L horizon material consistently displayed the lowest relative loss of mercury with heating from 60 to 225°C.

Mercury loss patterns for September samples were generally similar to those for the July samples (Figure 13). However, there was a greater relative and absolute loss of mercury with heating at the 50 to 150°C interval from L, F, and H samples collected in September compared to the same samples collected in July. As before, samples from the L

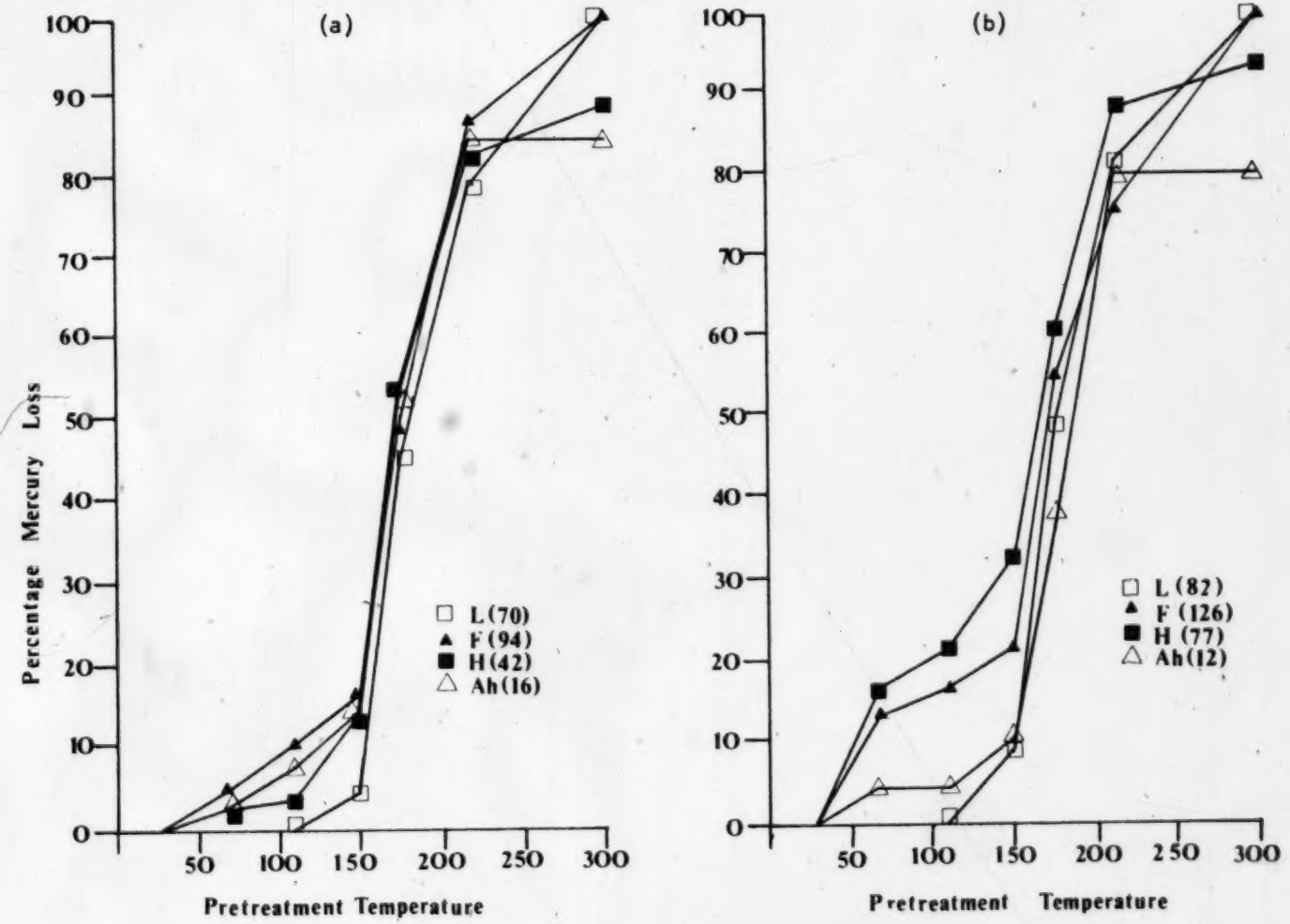

Figure 13. Mercury loss curves for (a) July and (b) September soil samples showing liberation of mercury with heating (values in brackets represent initial content of Hg).

horizon displayed lower relative losses of mercury at pretreatment temperatures of 60 to 150°C. Greater amounts of mercury were liberated from the L, F, and H samples than from the mineral containing Ah samples at heat pretreatments of 150 to 225°C.

Results of the pyrolysis experiment suggested that the samples contained a variety of mercury compounds and/or a variety of ways in which the element is bonded to organic constituents. The liberation of mercury from soil samples with heating occurred for the most part in a gradual manner rather unlike the results of Koksoy *et al.* (1967) for discrete inorganic mercury containing compounds. A broad spectrum of forms of mercury seems the most apparent reason for the overall gradual release characteristics.

The mercury loss curves for the September samples (Figure 13b) seem to consist of four general segments: one segment representing relative loss from room temperature up to the 60°C pretreatment temperature, another segment from 60 to 150°C, a third corresponding to the 150 to 225°C pretreatments, and the fourth for temperatures greater than 225°C.

Obviously, the first segment represents loss of the most volatile and/or weakly bonded forms of mercury. Species which most likely correspond to this low temperature segment include adsorbed elemental mercury and possibly methylated mercury. It is recognized that interpretation of this segment, like the others is not without ambiguity. The loss

of mercury within segments may reflect the presence of more than one mercury compound or alternatively, the gradual loss pattern may arise when only one form is present but chemically bonded with various strengths to organic and inorganic soil components.

Speculation on the form of mercury represented by the second loss segment (Figure 13a and b, 60 to 150°C) is based on the differential behavior in mercury loss between F, H, and Ah samples versus L samples and a consideration of the interpretation of the third segment (150 to 225°C). In the third segment, all samples lost the greatest absolute quantity of mercury and in a very similar fashion (based on the slopes of the lines). For L horizon samples, the third segment must correspond to the loss of that mercury which is chemically bonded to constituents within the leaf tissue. Available evidence indicates its form in raw plant tissue is largely as divalent mercury (rather than methylmercury) covalently bonded with nitrogenous and sulfhydral groups of proteins some of which occur as constituents of cell walls (Jernelov, 1969; Tripp and Harriss, 1978; Minagawa *et al.*, 1980). Since the samples of L horizon consist essentially of undecomposed leaf material, the bulk of mercury contained in such samples must occur in the same aforementioned forms and that these forms decompose liberating Hg° through the 150 to 225°C range. Since liberation of mercury from F, H, and Ah samples closely parallel the loss from the L sample for third temperature segment (e.g. Figure 13a), these same

forms (namely Hg^{2+} covalently bonded to S and N) likely contribute the major form of the element in all of the four studied surface horizons. If this explanation is accepted, then losses of mercury in the second temperature segment (60 to 150°C) likely represent forms largely other than S and N bonded Hg^{2+} since samples of L horizon display little loss of mercury with heating at temperatures less than 150°C. What these other forms are still remains to be clarified; their thermal stability is lower than covalently bonded mercury. Hence it seems probable that the forms would include adsorbed organomercurial compounds and/or mercury associated with humic materials.

Within the fourth temperature segment (225 to 300°C) little additional mercury was liberated from H and Ah samples with some mercury remaining after heating to 300°C. All mercury was liberated from samples composed strictly of organic material (L and F horizons) prior to or at 300°C. These results are indicative of the presence of a minor quantity of mercury (10 to 20% of total) contained within admixed mineral material in Ah and H samples as has been suggested by others for mineral soil samples (Dudas and Pawluk, 1976).

The major difference between September and July samples is in the quantity of mercury liberated with heating at 60°C (i.e. the first segment). The pyrolysis data shows the previously discussed elevated fall season values in FH horizons (pages 86 to 87) are indeed caused by adsorption of

volatile mercury forms onto the organic soil horizons in agreement with the data on emanations of gaseous mercury from soil (pages 58 to 62). In the section on mercury in aspen leaves (pages 38 to 46) it was shown mercury in aspen leaves reached its highest concentration in the fall season just when gaseous mercury emanations (as detected with copper foil) displayed maximum flux. This then lead to the suggestion (pages 44 to 45) that high levels in leaves was, in part, due to foliar adsorption of mercury emanating from the soil. Results of the pyrolysis experiment indicates this explanation involving foliar adsorption is rather tenuous since the L horizon, through which the emanating mercury must pass to reach the leaves on trees, is not a tenuous adsorbant of gaseous forms of mercury. There is no reason to believe fresh leaves on the trees should have a greater adsorption capacity than the slightly decomposed leaves of the L horizon. Consequently, it appears root uptake of gaseous mercury figures more prominently in explaining the fall season levels in aspen leaves.

V. SUMMARY

This research was done to further the understanding of the dynamic nature of mercury in two Alberta forested soils particularily in relation to a subcycle of the total global cycle of mercury as shown in Figure 14 (taken from Kothny, 1973). The cycle of mercury in nature is not totally understood since the biogeochemistry of the element is very complex as mercury occurs in numerous forms in the environment (solid, solute, gas, adsorbed vapor) and there is a constant cycling of mercury between the different environmental reservoirs.

The principal findings of this investigation were as follows:

1. Results of this study show normal background levels of mercury in forest soils fluctuate seasonally in a systematic manner. Levels of mercury in the surface soil horizons (L, F, H, and Ah) were relatively high in early spring, generally lower during June and July and decreased to minimum levels of mercury in August. Starting in August content of mercury increased dramatically to maximum levels in late September afterwhich levels declined towards summer values. The increased levels of mercury in September in litter layers coincides with the emanations of gaseous mercury during the fall season and appears related to seasonal changes in soil moisture and temperature. Levels of mercury were generally highest in the F horizon and

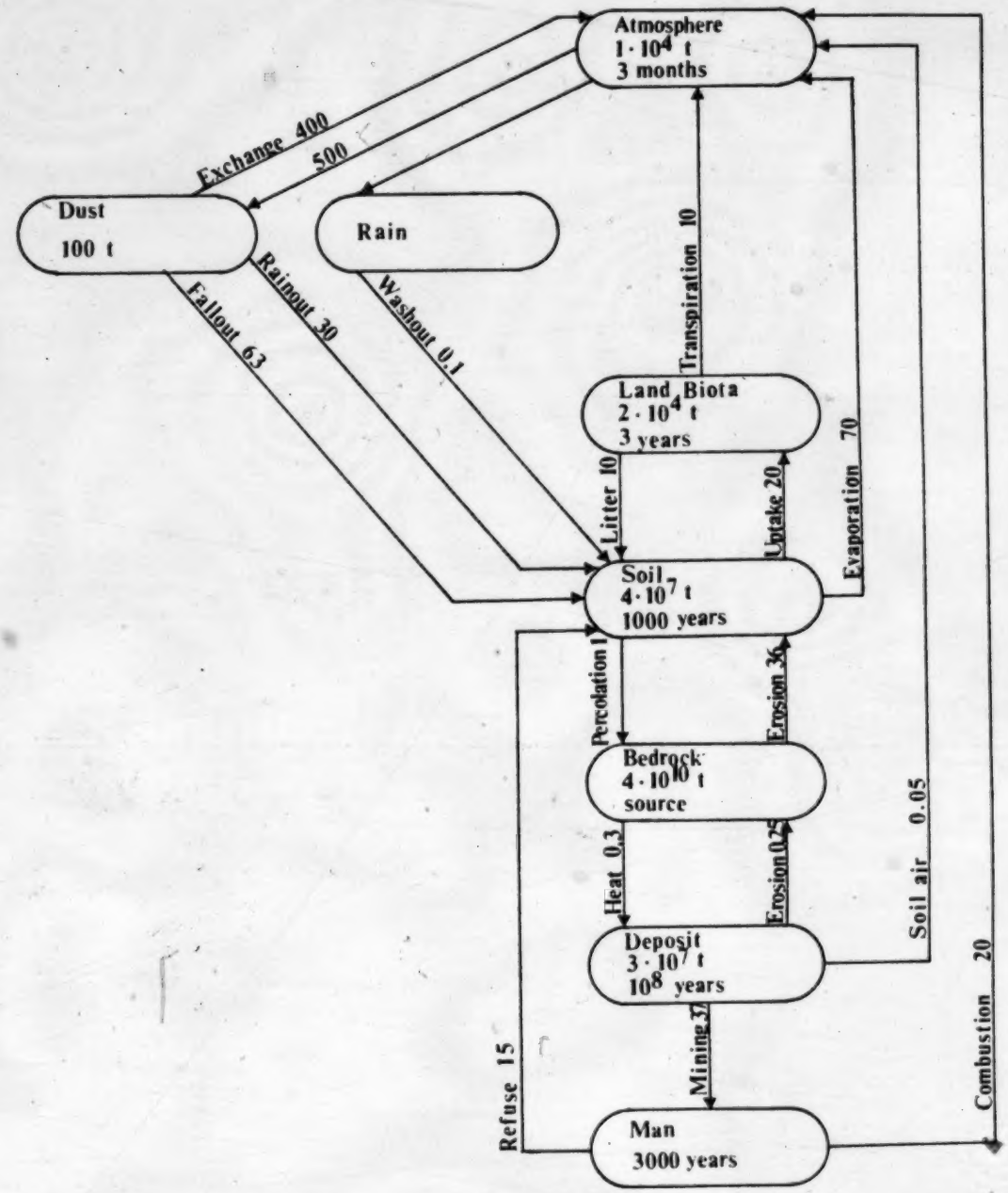

Figure 14. The cycle of mercury in nature. Residence times are in years and months. Numbers on routes are tons per day. Immobilized tonnage is indicated below each component. (taken after Kothny, 1973).

lowest in the Ah horizon at any given sampling date. In general, levels of mercury were higher in the L horizon than in the H horizon.

2. Elevated levels of mercury in forest litter are a transient feature occurring each fall season. These elevated levels appear to result from the absorption of vaporous mercury on organic matter of the surface soil horizons as it diffuses upward through the soil profile during the fall season. Originally, it was believed that litter layers of Luvisolic soils contained higher levels of mercury than grassland soils because of negative enrichment as the leaf material decomposed. The decomposition experiments, however, indicate that a net loss of mercury accompanies decomposition of organic debris. In previous studies where elevated levels of mercury were reported, sample collection probably occurred in the fall season.
3. Cycling of mercury occurs by the biota largely via vascular plants; role of non vascular plants is to increase mean residence time of mercury in organic layers thereby contibuting to levels higher than in grassland Ah horizons. Results of this study indicate that the majority of mercury added to the surface soil horizons occurred through the deposition of leaves of vascular plants at leaf fall.
4. Mercury was not detected in rainwater or canopy drip of this study, suggesting mercury addition via this source

to soils of the two study areas must have been less than the detection limit of the flameless AA method. As shown in Figure 14, washout of mercury by rainfall only accounts for a very minor amount of atmospheric mercury returned to the soil.

5. Return of mercury from the atmosphere to the soil by dry deposition of mercury on leaves must have also occurred in amounts below detection limits. Removal of atmospheric mercury by dust particles through rainout or fallout is the major process for return of atmospheric mercury to the soil (Figure 14). However, results of this investigation suggested that dry deposition was not a major process in the two study areas. Perhaps fallout of atmospheric mercury by dust was not adequately assessed in this study. Only two sampling events were involved to directly evaluate dry deposition; however, the more extensive measurements involving canopy drip also suggested that mercury input via dry deposition was less than what could be detected by the techniques and methods of this study. Mercury in the atmosphere likely returns to the soil by all known mechanisms such as dry deposition, rainfall, snowfall, and direct vapor adsorption. However, the amounts of mercury deposited onto the soil of the two study areas are at or below what could be detected with the methods and manner of sampling employed in this research.

6. Emanations of gaseous mercury were not detected during

most of the spring and summer but increased sharply during August and September. This flux of mercury decreased rapidly during October and was no longer detected in November. The fall release of gaseous mercury appears to be related to seasonal trends in soil moisture and temperature. The mercury emanations of coincides with the increased levels of mercury in litter layers and in aspen leaves during the fall season.

7. Results of the pyrolysis experiment suggest there is a variety of forms of mercury present in the surface soil horizons such as elemental, methylated, and divalent mercury and/or a variety of ways in which mercury can be bonded to organic constituents such as covalent and other various forms of chemical bonds.

Previous studies on soil mercury have dealt with static measurements to obtain background levels. These static measurements can be quite misleading, as this study indicates, because the mercury status in each of the surface soil horizons fluctuates during the seasons. Seasonal fluctuations and balance of mercury were assessed in this study and illustrate the dynamic behavior of mercury in litter layers of deciduous forested soils.

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APPENDICES

Appendix I. Content of mercury , carbon, and nitrogen in surface soil horizons and leaf samples.

SAMPLING DATE	SAMPLE*	Hg ppb	%C	%N	C/N
1/6/77	CL-Leaves-1	60	52	2.9	18
	2	32	46	3.0	15
	3	45	48	2.7	18
	4	52	48	2.7	18
	E-Leaves-1	45	50	2.8	18
	2	38	50	2.8	18
	3	43	50	2.6	19
	4	35	50	3.0	17
	CL-L-1	100	45	1.5	30
	2	95	48	1.6	30
	3	88	39	1.6	24
	4	83	43	1.6	27
	E-L-1	70	41	1.5	27

* CL- Cooking Lake study area

E- Ellerslie study area

1, 2, 3, 4- replicate number

Leaves- leaf samples

L- L horizon samples

F- F horizon samples

H- H horizon samples

Ahg- Ahg horizon samples

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	2	78	43	1.8	24
	3	75	37	1.6	23
	4	68	44	1.4	31
	CL-F-1	135	36	1.9	19
	2	143	39	1.9	21
	3	160	36	1.9	19
	4	113	14	1.8	18
	E-F-1	130	35	2.0	18
	2	105	40	2.2	18
	3	110	30	2.2	14
	4	136	34	2.5	14
	CL-H-1	60	18	1.4	13
	2	98	26	1.2	22
	3	45	6	0.5	12
	4	55	8	0.5	16
	E-H-1	85	41	2.1	210
	2	85	39	1.3	30
	3	25	15	2.6	6
	4	55	21	1.4	15
	E-Ahg-1	23	5	0.4	12
	2	34	3	0.3	10
	3	28	4	0.3	13
	4	23	3	0.3	10
15/6/77	CL-Leaves-1	35	50	2.6	19
	2	30	48	2.5	19

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	3	33	52	2.6	20
	4	30	51	2.7	19
	E-Leaves-1	30	50	2.8	18
	2	35	50	2.8	18
	3	25	48	3.0	16
	4	40	52	2.6	20
	CL-L-1	80	44	1.6	28
	2	63	46	1.4	33
	3	80	46	1.4	33
	4	90	44	1.5	29
	E-L-1	63	43	1.7	25
	2	55	42	1.6	26
	3	60	40	1.6	25
	4	65	42	1.5	28
	CL-F-1	120	43	1.6	27
	2	110	36	1.8	20
	3	80	23	1.2	19
	4	123	23	1.1	21
	E-F-1	85	37	1.2	31
	2	60	31	1.3	24
	3	65	34	1.2	28
	4	75	35	1.6	22
	CL-H-1	25	13	1.0	13
	2	53	20	0.8	25
	3	45	13	1.0	13

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	4	38	5	0.5	10
	E-H-1	34	39	2.9	13
	2	35	29	2.3	13
	3	70	36	2.4	15
	4	43	37	2.6	14
	E-Ahg-1	16	3	0.4	8
	2	15	6	0.6	10
	3	15	4	0.4	10
	4	24	5	0.4	13
29/6/77	CL-Leaves-1	34	52	2.4	22
	2	29	50	1.9	26
	3	30	49	2.3	21
	4	26	53	2.1	25
	E-Leaves-1	50	51	3.2	16
	2	30	52	2.4	22
	3	29	53	3.0	18
	4	30	51	2.6	20
	CL-L-1	70	45	1.8	25
	2	70	44	1.4	31
	3	95	47	1.7	28
	4	76	48	1.8	27
	E-L-1	67	43	2.0	22
	2	72	43	1.6	27
	3	65	44	1.7	26
	4	76	44	1.8	24

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	CL-F-1	100	38	0.6	63
	2	113	43	0.6	72
	3	108	23	0.8	29
	4	117	38	0.8	48
	E-F-1	73	33	2.6	13
	2	83	35	3.3	11
	3	90	36	2.4	15
	4	79	31	2.3	13
	CL-H-1	14	8	1.9	4
	2	47	11	1.8	6
	3	40	9	1.3	7
	4	31	10	1.7	6
	E-H-1	28	31	2.1	15
	2	65	29	1.8	16
	3	47	40	1.8	6
	4	47	36	2.0	18
	E-Ahg-1	9	2	0.2	10
	2	14	8	0.6	13
	3	19	5	0.5	10
	4	19	12	1.0	12
	CL-Leaves-1	28	47	2.4	20
	2	30	44	2.3	19
	3	32	47	2.6	18
	4	33	45	2.3	20
	E-Leaves-1	34	47	2.9	16

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	2	45	47	2.6	18
	3	44	49	2.9	17
	4	45	46	2.8	16
	CL-L-1	73	40	1.4	29
	2	85	40	1.8	22
	3	80	38	1.8	21
	4	61	41	1.9	22
	E-L-1	73	39	2.0	20
	2	66	36	2.2	16
	3	66	39	1.8	22
	4	66	40	1.7	24
	CL-F-1	109	31	2.2	14
	2	88	33	2.0	16
	3	80	25	1.9	13
	4	99	29	1.8	16
	E-F-1	78	25	2.0	13
	2	75	25	2.1	12
	3	73	28	2.1	13
	4	87	31	2.1	15
	CL-H-1	45	21	1.8	12
	2	85	18	1.3	14
	3	50	14	1.1	13
	4	48	11	0.8	14
	E-H-1	43	29	3.3	9
	2	59	32	2.5	13

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	3	59	23	2.1	11
	4	43	19	2.0	10
	E-Ahg-1	13	4	0.5	8
	2	22	4	0.4	10
	3	23	4	0.4	10
	4	21	4	0.4	10
27/7/77	CL-Leaves-1	56	47	2.5	19
	2	60	42	2.5	17
	3	37	43	2.5	17
	4	61	44	2.5	18
	E-Leaves-1	75	45	2.4	19
	2	46	48	2.1	23
	3	68	47	2.3	20
	4	45	48	2.2	22
	CL-L-1	79	40	1.8	22
	2	89	35	1.9	18
	3	87	35	1.6	22
	4	75	41	1.9	22
	E-L-1	47	40	1.6	25
	2	55	35	1.7	21
	3	55	41	1.9	22
	4	60	39	1.7	23
	CL-F-1	87	30	2.1	14
	2	100	36	2.1	17
	3	67	29	1.6	18

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	4	100	34	2.1	16
	E-F-1	84	24	2.5	10
	2	87	28	2.2	13
	3	88	27	2.1	13
	4	73	26	2.2	12
	CL-H-1	47	19	2.8	7
	2	50	13	1.0	13
	3	47	14	0.9	16
	4	89	17	1.1	15
	E-H-1	79	29	2.3	13
	2	75	27	2.5	11
	3	75	26	1.8	14
	4	73	31	1.7	18
	E-Ahg-1	22	3	0.3	10
	2	16	6	0.6	10
	3	16	5	0.4	13
	4	9	3	0.3	10
10/8/77	CL-Leaves-1	32	47	2.3	20
	2	72	42	2.3	18
	3	41	47	2.5	19
	4	30	49	2.4	20
	E-Leaves-1	34	48	2.0	24
	2	43	47	2.0	24
	3	32	47	2.6	18
	4	55	53	2.3	23

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	CL-L-1	116	42	1.6	26
	2	72	38	1.8	21
	3	57	39	1.5	26
	4	57	40	1.9	21
	E-L-1	66	38	1.7	22
	2	46	39	1.7	23
	3	53	37	1.8	21
	4	66	38	1.7	22
	CL-F-1	64	42	2.0	21
	2	73	37	2.0	18
	3	59	39	1.8	22
	4	71	35	1.8	19
	E-F-1	44	34	1.9	18
	2	77	36	1.9	19
	3	48	31	1.9	16
	4	66	30	2.2	14
	CL-H-1	73	19	1.3	15
	2	53	18	1.0	18
	4	25	9	0.6	15
	E-H-1	41	35	2.1	17
	2	48	42	1.7	25
	3	24	33	2.8	12
	4	34	40	3.0	13
	E-Ahg-1	15	4	0.5	13
	2	26	2	0.2	10

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	3	7	1	0.2	5
	4	17	3	0.3	10
8/9/77	CL-Leaves-1	41	40	1.3	31
	2	69	36	1.3	28
	3	68	40	1.4	29
	4	53	40	1.3	31
	E-Leaves-1	69	42	1.5	28
	2	54	40	1.6	25
	3	106	47	1.4	34
	4	83	43	1.3	33
	CL-L-1	68	40	1.6	25
	2	106	41	1.8	23
	3	65	36	1.6	22
	4	100	36	2.1	17
	E-L-1	91	36	2.0	18
	2	44	36	1.4	26
	3	59	40	1.4	29
	4	83	38	2.0	19
	CL-F-1	120	40	2.0	20
	2	147	35	1.9	18
	3	161	38	2.1	18
	4	109	40	1.8	22
	E-F-1	123	34	2.2	15
	2	126	34	2.2	15
	3	129	35	2.3	15

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	4	147	34	2.1	16
	CL-H-1	41	13	0.7	19
	2	125	20	0.8	25
	3	83	24	0.7	34
	4	56	8	0.7	11
	E-H-1	68	37	2.1	18
	2	59	36	2.0	18
	3	62	37	2.2	17
	4	74	31	2.1	15
	E-Ahg-1	14	3	0.4	8
	2	22	4	0.4	10
	3	13	4	0.3	13
	4	14	4	0.3	13
27/9/77	CL-L-1	162	37	1.6	23
	2	112	42	1.5	28
	3	118	42	1.4	30
	4	88	42	1.4	30
	E-L-1	192	43	1.8	24
	2	66	44	1.4	31
	3	60	37	1.5	25
	4	107	41	1.4	29
	CL-F-1	99	27	1.5	18
	2	105	34	1.7	20
	3	72	31	1.6	19
	4	102	39	1.9	21

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	E-F-1	107	36	2.1	17
	2	85	38	2.0	19
	3	84	37	2.1	18
	4	102	34	2.1	16
	CL-H-1	58	14	0.9	16
	2	32	7	0.4	18
	3	29	10	0.6	17
	4	60	9	0.7	13
	E-H-1	74	38	2.2	17
	2	70	39	2.5	16
	3	56	37	2.0	18
	4	77	26	1.6	16
	E-Ahg-1	21	6	0.5	12
	2	20	4	0.3	13
	3	23	7	0.6	12
	4	22	6	0.5	12
18/12/77	CL-L-1	78	29	1.6	18
	2	82	30	1.7	18
	4	59	35	1.5	23
	E-L-1	60	30	1.2	25
	2	51	37	1.3	28
	CL-F-1	64	19	1.3	15
	2	53	4	0.5	8
	4	82	31	2.0	16
	E-F-1	83	33	2.2	15

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	2	106	33	2.1	16
	3	79	30	2.0	15
	CL-H-1	42	7	1.0	7
	2	79	32	1.8	18
	4	92	23	1.7	14
	E-H-1	76	29	2.2	13
	2	55	30	2.0	15
	3	56	27	2.1	13
3/5/78	CL-L-1	65	35	1.8	19
	2	116	45	1.8	25
	3	95	41	1.8	23
	4	72	37	1.8	21
	E-L-1	60	41	1.2	34
	2	72	42	1.1	38
	3	64	37	1.9	19
	4	59	41	1.4	29
	CL-F-1	103	35	2.2	16
	2	140	28	2.0	14
	3	101	34	1.8	19
	4	146	35	2.1	17
	E-F-1	87	33	2.1	16
	2	92	35	2.1	17
	3	117	32	2.1	15
	4	116	35	2.1	17
	CL-H-1	93	30	1.8	17

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	2	85	13	0.8	16
	3	64	8	0.8	10
	4	54	15	0.7	21
	E-H-1	85	36	2.5	14
	2	87	40	2.4	17
	3	76	41	3.0	14
	4	65	41	2.6	16
29/8/78	CL-L-1	93	28	1.9	15
	2	78	36	1.6	22
	3	73	32	1.4	23
	4	63	35	1.8	19
	E-L-1	63	36	1.9	19
	2	64	33	1.9	19
	3	89	34	1.6	21
	CL-F-1	116	33	1.7	21
	2	101	35	1.7	21
	3	89	34	1.7	20
	4	98	35	1.9	18
	E-F-1	45	30	2.0	15
	2	100	35	2.1	17
	3	105	31	2.1	15
	CL-H-1	103	32	2.0	16
	2	66	23	1.3	18
	3	61	23	1.3	18
	4	60	19	0.9	21

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	E-H-1	35	36	0.9	40
	2	38	20	1.5	13
	3	57	36	2.4	15
15/9/78	CL-L-1	106	33	1.8	18
	2	113	29	1.8	16
	3	104	28	1.9	15
	4	110	31	1.7	18
	E-L-1	110	29	1.7	17
	2	113	29	1.8	16
	3	106	30	1.8	17
	CL-F-1	120	27	2.1	13
	2	161	28	2.0	14
	3	140	25	2.0	12
	4	110	28	2.0	14
	E-F-1	128	29	2.0	14
	2	126	29	2.2	13
	3	133	30	2.2	14
	CL-H-1	75	15	1.2	12
	2	80	12	1.0	12
	3	79	10	1.0	10
	4	79	8	1.0	8
	E-H-1	75	14	1.1	13
	2	83	14	1.4	10
	3	80	14	1.2	12
29/9/78	CL-L-1	68	32	1.8	18

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	2	80	30	1.9	16
	3	58	32	1.6	20
	4	90	27	1.7	16
	E-L-1	76	35	1.6	22
	2	77	31	1.7	18
	3	58	29	1.8	16
	CL-F-1	100	26	2.2	12
	2	100	29	1.7	17
	3	102	27	2.0	14
	4	95	33	1.9	17
	E-F-1	11	25	2.2	11
	2	93	28	2.1	13
	3	83	22	2.1	10
	CL-H-1	55	14	1.2	12
	2	53	13	0.9	14
	3	40	3	1.0	3
	4	81	7	1.1	6
	E-H-1	21	11	1.0	11
	2	23	17	1.7	10
	3	25	13	1.6	8

Appendix II. Content of mercury, carbon, and nitrogen in decomposing leaf samples.

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
3/5/78	CL-Initial-1	75	38	1.1	35
	2	87	30	1.0	30
	3	80	30	0.9	33
	4	75	34	0.8	43
	E-Initial-1	76	39	1.0	39
	2	55	32	1.1	29
	3	88	31	1.1	28
	CL-Field-1	62	35	1.0	35
	2	48	33	0.8	41
	3	53	36	1.0	36
	4	59	43	0.9	48
	E-Field-1	107	40	1.8	22
	2	63	34	0.9	38
	3	42	28	0.8	35
12/5/78	CL-Field-1	77	38	1.3	29
	2	72	28	1.0	28
	3	55	34	1.1	31
	4	39	30	1.0	30

* Field = field samples

-N = samples without added nitrogen

+N = samples with added nitrogen

NLD = new leaf decomposition study

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	E-Field-1	39	32	1.0	30
	2	46	32	1.0	32
	3	80	29	1.1	26
15/5/78	CL -N-1	33	41	0.8	51
	2	39	39	0.9	43
	3	37	40	1.0	40
	4	67	36	0.8	45
	E -N-1	39	36	1.0	36
	2	45	41	0.9	46
	3	41	42	0.7	60
	CL +N-1	39	41	0.8	51
	2	65	42	0.9	47
	3	41	44	0.9	49
	4	39	40	0.9	44
	E +N-1	52	40	0.8	50
	2	88	42	0.8	52
	3	51	31	0.8	39
29/5/78	CL-Field-1	39	36	1.1	33
	2	42	36	0.9	40
	3	45	35	0.9	39
	4	76	41	1.1	37
	E-Field-1	83	35	1.0	35
	2	81	36	0.9	40
	3	73	38	1.3	29
	CL -N-1	64	44	0.9	49

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	2	71	31	1.0	31
	3	79	42	1.1	38
	4	78	36	0.9	40
	E -N-1	84	42	1.0	42
	2	116	41	0.9	46
	3	61	42	0.8	52
	CL +N-1	66	45	0.9	50
	2	61	44	1.0	44
	3	47	40	1.2	33
	4	42	44	1.0	44
	E +N-1	56	42	1.0	42
	2	56	40	1.0	40
	3	39	35	0.8	44
12/6/78	CL-Field-1	76	36	1.2	30
	2	73	39	1.0	39
	3	76	34	0.9	38
	4	38	43	1.3	33
	E-Field-1	59	36	1.0	36
	2	50	36	1.1	33
	3	44	40	0.9	44
	CL +N-1	54	42	0.9	47
	2	56	40	1.2	33
	3	78	39	1.0	39
	4	49	35	1.0	35
	E +N-1	56	42	1.0	42

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	2	69	34	1.0	34
	3	54	35	1.3	27
	CL -N-1	63	36	0.9	40
	1	167	39	1.4	28
	3	60	39	1.4	28
	4	68	39	1.2	32
	E -N-1	145	42	1.4	30
	2	63	41	1.4	29
	3	56	38	0.8	48
4/7/78	CL-Field-1	64	38	1.2	32
	2	78	41	1.3	32
	3	74	41	1.1	37
	4	101	44	1.2	37
	E-Field-1	69	40	1.0	40
	2	69	32	1.1	29
	3	73	41	1.3	32
	CL +N-1	108	45	0.9	50
	2	67	43	1.2	36
	3	74	40	1.5	27
	4	83	42	0.8	52
	E +N-1	69	39	1.0	39
	2	104	41	1.1	37
	3	108	43	1.0	43
	CL -N-1	64	46	1.0	46
	2	74	42	1.2	35

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	3	74	43	1.2	36
	4	54	49	1.0	49
	E -N-1	116	40	1.3	31
	2	62	40	1.3	31
	3	64	41	0.9	46
	CL-Field-1	56	39	1.1	35
	2	67	42	1.3	32
	3	68	39	0.9	43
	4	61	31	1.1	28
	E-Field-1	61	38	1.0	38
	2	63	36	0.9	40
	3	77	40	1.4	29
	CL +N-1	58	43	1.0	43
	2	58	41	1.1	37
	3	62	43	1.4	31
	4	54	43	1.0	43
	E +N-1	65	42	1.5	28
	2	86	41	1.4	29
	3	65	34	1.1	31
	CL -N-1	50	41	1.2	34
	2	71	41	1.2	34
	3	81	43	1.3	33
	4	63	32	1.2	36
	E -N-1	80	43	1.2	36
	2	88	43	1.1	39

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	3	58	43	0.9	48
	CL-Field-1	67	37	1.4	26
	2	71	31	1.3	24
	3	75	36	1.0	36
	4	62	38	1.1	35
	E-Field-1	62	33	1.1	30
	2	53	36	1.4	26
	3	75	31	1.5	21
	CL +N-1	132	38	1.0	38
	2	92	39	1.2	32
	3	97	36	1.3	28
	4	84	33	1.0	33
	E +N-1	103	38	1.2	32
	2	92	41	1.1	37
	3	83	33	1.1	30
	CL -N-1	94	34	1.0	34
	2	97	40	1.2	33
	3	85	41	1.4	29
	4	71	36	1.2	30
	E -N-1	107	39	1.1	35
	2	118	41	1.3	32
	3	100	36	1.0	36
23/8/78	CL-Field-1	48	26	1.0	26
	2	45	29	1.1	26
	3	50	36	1.3	33

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	4	44	39	1.0	29
	E-Field-1	52	26	1.4	19
	2	51	29	1.0	29
	3	47	32	1.4	23
	CL +N-1	84	33	1.1	30
	2	73	30	1.2	25
	3	88	31	0.9	34
	4	96	36	1.1	33
	E +N-1	103	33	1.4	24
	2	88	34	1.3	26
	3	85	31	1.0	31
	CL -N-1	85	35	1.3	27
	2	88	36	1.2	30
	3	91	38	1.4	27
	4	97	33	1.5	22
	E -N-1	78	31	1.3	24
	2	88	33	1.3	25
	3	92	35	1.1	32
29/9/78	CL-Field-1	73	31	1.3	24
	2	58	28	1.1	25
	3	51	27	1.0	27
	4	45	34	1.1	31
	E-Field-1	74	30	1.5	20
	2	50	31	1.5	21
	3	55	32	1.6	20

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	CL +N-1	107	33	1.3	25
	2	120	33	1.4	24
	3	135	32	1.6	20
	4	114	34	1.2	28
	E +N-1	117	35	1.6	22
	2	108	34	1.4	24
	3	116	34	1.2	28
	CL -N-1	113	33	1.4	24
	2	104	34	1.2	28
	3	122	32	1.6	20
	4	104	33	1.2	28
	E -N-1	103	34	1.3	26
	2	124	32	1.4	23
	3	119	36	1.2	30
17/11/78	E -N-1	153	36	1.3	28
	2	163	36	1.6	20
	3	155	35	1.6	22
	CL -N-1	163	35	2.1	17
	2	173	38	1.9	20
	3	169	36	2.3	16
	4	160	36	1.1	33
	E +N-1	164	34	2.0	17
	2	122	36	1.9	19
	3	178	37	1.5	25
	CL +N-1	163	35	1.6	22

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	2	167	33	1.8	18
	3	173	37	1.9	19
	4	125	35	1.7	21
3/1/79	E -N-1	196	35	2.0	18
	2	183	37	1.9	19
	3	202	38	1.6	24
	CL -N-1	180	36	1.6	24
	2	210	36	1.8	20
	3	181	35	2.0	18
	4	183	37	1.6	23
	E +N-1	199	37	2.0	18
	2	207	36	1.7	21
	3	180	34	1.5	23
	CL +N-1	186	33	1.5	22
	2	178	36	1.8	20
	3	174	40	2.0	20
	4	162	40	1.7	24
1/3/79	E -N-1	237	39	1.8	22
	2	210	38	2.0	19
	3	229	37	1.7	22
	CL -N-1	212	40	1.8	22
	2	363	41	1.9	22
	3	316	36	2.0	18
	4	230	40	2.0	20
	E +N-1	238	31	2.1	15

SAMPLING DATE	SAMPLE	Hg ppb	%C	%N	C/N
	2	237	38	2.0	19
	3	418	34	1.7	20
	CL +N-1	225	40	1.8	22
	2	256	37	1.8	21
	3	226	35	2.1	17
	4	180	37	1.8	21
30/4/79	E -N-1	295	30	1.9	16
	2	274	31	2.3	13
	3	265	32	2.4	13
	CL -N-1	251	35	2.1	17
	2	270	34	2.1	16
	3	225	30	2.0	15
	4	254	34	2.1	16
	E +N-1	230	27	2.0	14
	2	240	29	2.0	14
	3	266	31	1.9	18
	CL +N-1	217	32	1.8	18
	2	236	30	1.9	16
	3	215	32	2.1	15
	4	216	30	1.9	16

APPENDIX III. Results of pyrolysis experiment.

Table 1. Mercury loss for soil samples showing liberation of mercury with heating.

Sample	% loss Hg at						
Hg at 22C	60C	105C	150C	175C	210C	220C	300C
L 70	0	0	4	45	78	-	-
F 94	4	10	16	48	86	-	
H 42	2	3	14	52	82	-	88
Ah 16	2	7	14	53	84	-	84

Hg = ppb

Table 2. Mercury loss for soil samples (with elevated levels of mercury) showing liberation of mercury with heating.

Sample		% total loss Hg at						
	Hg at 22C	60C	105C	150C	175C	210C	220C	300C
L	82	0	0	9	48	81	92	
F	126	13	16	21	54	75	95	
H	77	16	21	32	60	87	92	93
Ahg	12	4	4	10	36	79	74	79

Hg = ppb